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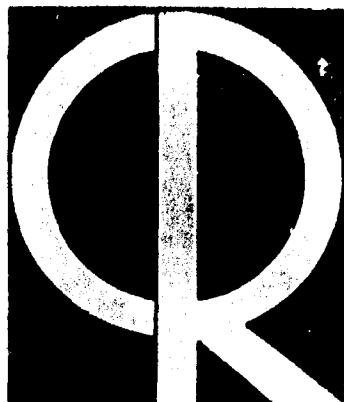


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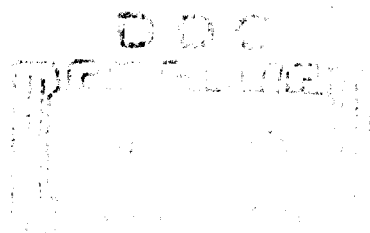
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Environmental Research Papers  
No. 24



The Infrared Telluric Absorption Spectrum Introductory Report

J.N. HOWARD  
J.S. GARING



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**The Infrared Telluric Absorption Spectrum Introductory Report**

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OPTICAL PHYSICS LABORATORY PROJECT 7670

AIR FORCE CAMBRIDGE RESEARCH LABORATORIES, OFFICE OF AEROSPACE RESEARCH, UNITED STATES AIR FORCE, L.G. HANSCOM FIELD, MASS.

# LES SPECTRES INFRAROUGES DES ASTRES

(RÉGION :  $1\ \mu$  À 3 mm)

## 29. — THE INFRARED TELLURIC ABSORPTION SPECTRUM INTRODUCTORY REPORT

J. N. HOWARD and J. S. GARING  
*Air Force Cambridge Research Laboratories*  
*Bedford, Mass., U. S. A.*

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## 29. — THE INFRARED TELLURIC ABSORPTION SPECTRUM INTRODUCTORY REPORT

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### ABSTRACT

Recent work on the infrared transmission spectrum of the atmosphere of the earth is reviewed and discussed. The principal laboratory effort has been studies of absorption bands of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and  $\text{O}_3$  in « synthetic » or simulated atmospheres, in which nitrogen or oxygen is used as the foreign gas under controlled conditions of concentration, pressure and path length. Some recent open air studies from balloons and high altitude aircraft are described, and the principal techniques of estimating open air slant path transmission from the laboratory data are described.

### LABORATORY TRANSMISSION STUDIES

For many years when one considered atmospheric infrared transmission, calculations were based on data taken at the Smithsonian Institution in the early 1900's by Fowle <sup>(1)</sup>, or else were based on one figure of the near infrared transmission in an overwater path across the Wash, England, containing 1.7 precipitable centimeters of water published by Gebbie, Harding, Hilsum, Price and Roberts <sup>(2)</sup> in the late 1940's. These data left much to be desired : it was difficult to separate the attenuation of the beam due to scattering by aerosols from the attenuation due to molecular band absorption ; it was difficult to be certain that the absorbing constituents were uniformly distributed along the absorption path ; and it was virtually impossible to extrapolate such data to predict conditions at other than ground level atmospheric pressure.

In the late 1940's Herzberg constructed at Yerkes Observatory a 22-meter multiple-traversal cell of the type designed by John White <sup>(3)</sup> in order to obtain laboratory spectra of weak bands of molecules. His spectra were obtained in the spectral regions acces-

sible photographically. In 1948 Migeotte duplicated the 22-meter multiple-traversal cell at Ohio State University with the intention of extending absorption studies into the infrared. This project was continued by Howard, Burch and Williams, who published a series of papers (4) on the infrared absorption bands of water vapor and carbon dioxide in « synthetic » atmospheres of nitrogen or oxygen.

With a sample of  $\text{CO}_2$  or  $\text{H}_2\text{O}$  in the multiple-traversal cell a spectrum was run of a given absorption band as the path length was varied in steps of 88 meters (corresponding to 4 traversals of the cell), from a minimum path of 88 meters to a maximum of about 2 km. The band being studied was recorded at each path length, and then dry nitrogen (or oxygen) was added to a new total pressure and the process repeated. This was a slow study, as a set of runs on a given band as a function of path length and total pressure generally required one or two days, and for each band such runs were made for many different samples of gas. Runs also had to be made with the cell empty, and changing to a new spectral region usually involved changing to a different prism in the spectrometer or different windows on the cell. The experimental portion of this study, the calibration of the apparatus and the re-plotting and reduction of the data required about three years of effort. The spectra were planimetered and the results presented in the form of empirical fits relating the total absorptance of the sample,  $\int A_\nu d\nu$ , to the concentration,  $w$ , partial pressure of the sample,  $p$ , and the total pressure,  $P$ , of the synthetic atmosphere. In an effort to assist other workers who desired the observed spectral contour or who wished to test a different theoretical fit, all of the details of the data obtained were presented in the curves and tables of the report of this work by Howard, Burch and Williams, which was published in 1955.

It soon became apparent that many workers found such data useful, although there was considerable demand for better resolution of the spectral contour of the bands and a desire for more data for absorption paths shorter than the 88 meter minimum path of the



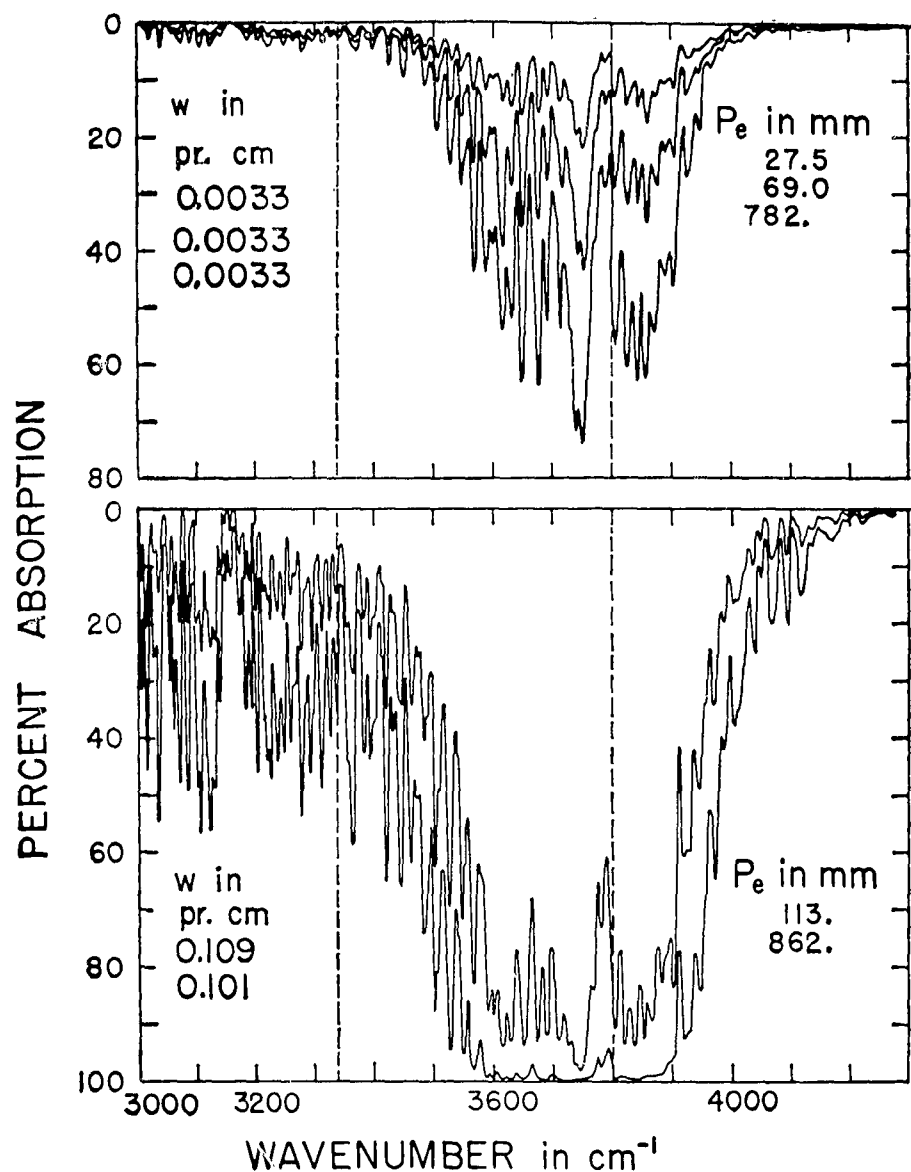


Fig. 1. — Laboratory absorptance measurements of the water vapor bands at 2.7 microns.

Howard, Burch and Williams apparatus. In 1955 Burch commenced a new series of experiments on absorption in synthetic atmospheres with many improvements over the previous work. These results are now published (5).

The spectrometer employed a double beam system, each beam

containing a multiple-traversal cell. This permitted a direct recording of percent absorption versus wavenumber, so that data reduction was considerably simplified. The mirrors of the multiple-traversal cells were spaced one meter apart, with available paths from 4 to 40 meters in steps of 4 meters, and the aperture of the cell matched that of the spectrometer. This greatly improved the resolution of the spectrum. The cells could be pressurized to about 6 atm and the temperature could be controlled between 20°C and 70°C, so that some studies could be made on temperature dependence on absorption.

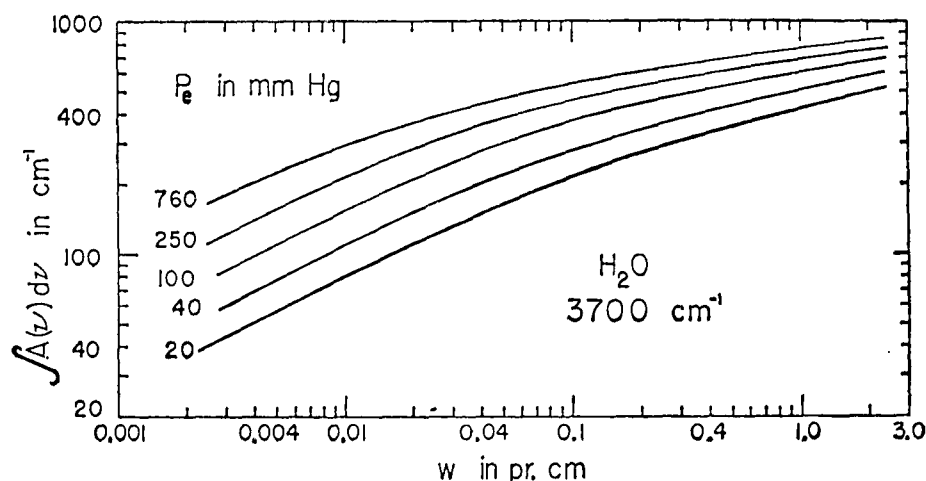


Fig. 2. — Observed total absorptance of the 2.7 micron water vapor bands as a function of pressure and absorber concentration.

Fig. 1 is a typical set of curves of water vapor in the 2.7  $\mu$  region and Fig. 2 relates the area under each curve,  $\int A_\nu d\nu$ , to the absorber concentration and the pressure. Tables I and II compare the range of concentrations and the number of individual spectra obtained by Burch with the earlier data of Howard et al. for carbon dioxide and water vapor, and Table III lists the additional bands studied of CO, CH<sub>4</sub> and N<sub>2</sub>O.

The improved double beam apparatus of Burch has permitted some additional studies that were not practical with the earlier apparatus. For example, it was possible experimentally to determine

the self-broadening coefficients for the gases studied. It is well known that the self-broadening effects on a spectral band are stronger than the so-called Lorentz or collision broadening between the absorbing molecule and molecules of a diluent, or foreign gas, which has no spectral absorption in the same spectral region. Thus, if we put into the reference beam of a double beam spectrometer a short path of a pure sample of an absorbing gas at a partial pressure  $p^{\text{ref}}$ ,

TABLE I

*A summary of the total absorptance measurements of carbon dioxide made at Ohio State University.*

Band $\mu$	No. Runs		Concentration, atmos — cm	
	Burch	Howard	Burch	Howard
1.4		13		432 — 8090
1.6		13		432 — 8090
2.0		35		432 — 8090
2.7	54	148	0.08 — 24	11 — 1620
4.3	94	115	0.005 — 23	9 — 1565
4.8		42		9 — 1565
5.2		11		46 — 1565
9.4	42		48 — 11,200	
10.4	42		48 — 11,200	
15.	195	49	0.005 — 11,200	3 — 513

TABLE II

*A summary of the total absorptance measurements of water vapor made at Ohio State University.*

Band $\mu$	No. Runs		Concentration, pr. cm	
	Burch	Howard	Burch	Howard
0.94		12		9.91 — 3.85
1.1		44		0.01 — 3.85
1.38		60		0.01 — 3.85
1.87	42	137	0.003 — 0.11	0.01 — 3.85
2.7	46	169	0.003 — 0.11	0.002 — 2.4
3.2	46	169	0.003 — 0.11	0.002 — 2.4
6.3	33	103	0.002 — 0.07	0.02 — 1.2

and then put a much smaller pressure  $p$  of the same kind of absorbing gas into the sample cell, but at a longer path length, such that the number of molecules (the «absorber concentration») is the same in both paths, we will find considerably less absorption in the sample cell. If we now add nitrogen (the broadening gas) at pressure  $p_b$  until the absorptions in the sample and reference beams are most nearly equal, we can write  $Bp^{\text{ref}} = p_b + Bp$  and, solving for  $B$ , the self-broadening coefficient, we obtain  $B = \frac{p_b}{p^{\text{ref}} - p}$ ,

TABLE III

*A summary of the total absorbance measurements of CO, N<sub>2</sub>O and CH<sub>4</sub> made at Ohio State University.*

	Band cm <sup>-1</sup>	Concentration atmos — cm	Runs
CO	2143	0.001 — 46	179
	4260	37. — 1140	45
N <sub>2</sub> O	2224	0.0002 — 76	224
	2563	0.07 — 76	26
	2461		
	1285 1167	0.75 — 189	55
CH <sub>4</sub>	692 589	0.1 — 359	39
	3020	0.015 — 188	142
	1550	0.015 — 188	32
	1306	0.015 — 188	142

Table IV shows the self-broadening coefficients as determined by Burch for H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, CO.

Similarly, the same double beam apparatus could be used to determine the foreign-broadening coefficients and molecular cross

sections, both relative to nitrogen, for a variety of other broadening gases. This is shown in Table V. It was also possible to determine the band intensities of many bands, as shown in Table VI.

TABLE IV  
*Self-broadening coefficients of atmospheric molecules.*

	Band cm <sup>-1</sup>	Investigator	Self-Broadening Coefficient, B
N <sub>2</sub> O	2224, 1285, 1167	Burch	1.12 ± 0.07
	1285	Goody and Wormell	1.27 ± 0.04
	1167	Goody and Wormell	1.35 ± 0.07
	2224	Cross and Daniels	1.29
CO	2143	Burch	1.02 ± 0.06
	4260	Burch	1.08 ± 0.06
CH <sub>4</sub>	3020	Burch	1.30 ± 0.08
	1306	Burch	1.38 ± 0.08
CO <sub>2</sub>	3716, 3609, 2350	Burch	1.30 ± 0.08
	1064, 961, 667	Edwards	2
H <sub>2</sub> O	5332, 3756, 1595	Burch	5 ± 1.5
	500 cm <sup>-1</sup> region	Palmer	6 — 11
	4025.4 (line)	Vasilovsky and Neporant	6
	500-600 cm <sup>-1</sup>	Izatt	3.6 — 5.5

Burch and Williams also determined, as had HBW earlier, empirical relationships between the total absorptance,  $\int A_\nu d\nu$  and the absorber concentration  $w$ , absorber partial pressure  $p$ , and the total pressure  $P$ . The Burch report, which had a much more accurate representation for the self-broadening coefficient  $B$ , presented the pressure effect in terms of an equivalent pressure  $P_e$ , where

$$P_e = P + (B - 1)p$$

As in the earlier HBW report, a useful feature of the Burch report is that all of the total absorptance, concentration, pressure

and temperature data are presented in the curves and tables of the report for those who would prefer to attempt their own theoretical fit to the data.

TABLE V

*Foreign-Gas broadening coefficients, relative to nitrogen,  
for atmospheric molecules*

Band (cm <sup>-1</sup> )	Absorber Partial Pressure (mm Hg)	Total Pressure Range (mm Hg)	Broadener	Foreign Gas Broadening Coefficient	Relative Molecular Cross Section
N <sub>2</sub> O 2224	10	25-1000	He	0.73	0.58
			O <sub>2</sub>	0.83	0.93
			Ar	0.78	0.93
			H <sub>2</sub>	1.23	0.64
			CH <sub>4</sub>	1.08	0.94
N <sub>2</sub> O 1285	100	180-1000	He	0.70	0.57
			O <sub>2</sub>	0.72	0.87
			Ar	0.83	0.96
			H <sub>2</sub>	1.21	0.64
			CO <sub>2</sub>	1.17	1.14
CO 2143	100	200-3000	He	0.64	0.56
			Ar	0.78	0.92
			H <sub>2</sub>	0.85	0.56
			CH <sub>4</sub>	1.12	0.98
CO <sub>2</sub> 2350	50	80-700	He	0.59	0.52
			O <sub>2</sub>	0.81	0.92
			Ar	0.78	0.93
			H <sub>2</sub>	1.17	0.62
C <sub>2</sub> H <sub>4</sub> 3000	10	50-1000	He	0.52	0.51
CH <sub>4</sub> 3020	50	100-2500	He	0.56	0.56
			Ar	0.82	0.93
			CO <sub>2</sub>	1.25	1.15

TABLE VI

*Band intensities of atmospheric molecules*

Band (cm <sup>-1</sup> )	Burch	Other Workers	
N <sub>2</sub> O	2224	1850	1867 Thorndike and Wells
			1617 Callomon, McKean, Thomson
			1650 Eggers and Crawford
	2563	44 ± 6	
	2461	11.5 ± 1.5	
	1285		383 Wilson et al.
			265 ± 5 Goody and Wormell
			245 Eggers and Crawford
	1167	12 ± 1.2	10.9 ± 0.9 Goody and Wormell
			8.5 Eggers and Crawford
CH <sub>4</sub>	589	33 ± 4	40 Wilson et al.
			Eggers and Crawford
	3020	320 ± 48	360 Welsh, Pashler and Dunn
	1306	185 ± 28	157 Welsh and Sandiford
	1550	2.5 ± 0.5	
CO	2143	260 ± 26	237 Penner and Weber

The Ohio State University data referred to above represent the largest collection of such data arranged for easy intercomparison. Some additional CO<sub>2</sub> data, particularly for higher temperatures, have been measured by Edwards (6). Palmer (7) has made a very valuable study of the pure rotational band of water vapor, utilizing the long path cell at Johns Hopkins University. Figure 3 presents Palmer's curve of the amount of water vapor required to give a transmission of 50 %, as a function of wavenumber between 200 and 500 cm<sup>-1</sup> and Fig 4 shows the overall fit of the Palmer data to the statistical model of band transmission.

It is very difficult to make total absorptance measurements of this sort on the bands of ozone because of the unstable nature of

the molecule. Some early results were reported by Summerfield (8) and have been used in some calculations even though there was considerable doubt about the ozone concentration. There now exists

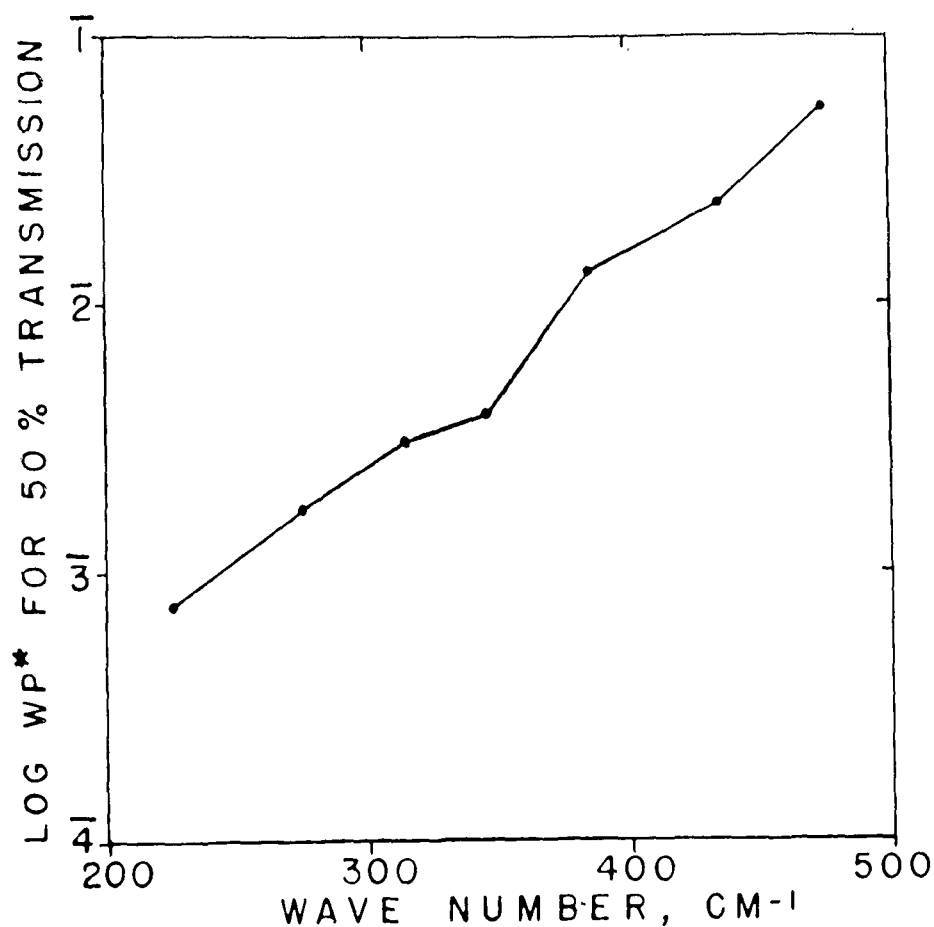


Fig. 3. — The amount of water vapor required to give 50 % transmission in the pure rotation band as a function of wavenumber.

however, a substantial body of data on ozone, published by Walshaw (9). Altshuler (10) has prepared charts from the Walshaw data which permit estimation of the absorptance of the 4.7 and 9.6 micron bands for atmospheric conditions. This should provide a very useful store of atmospheric absorption data for many years to come.



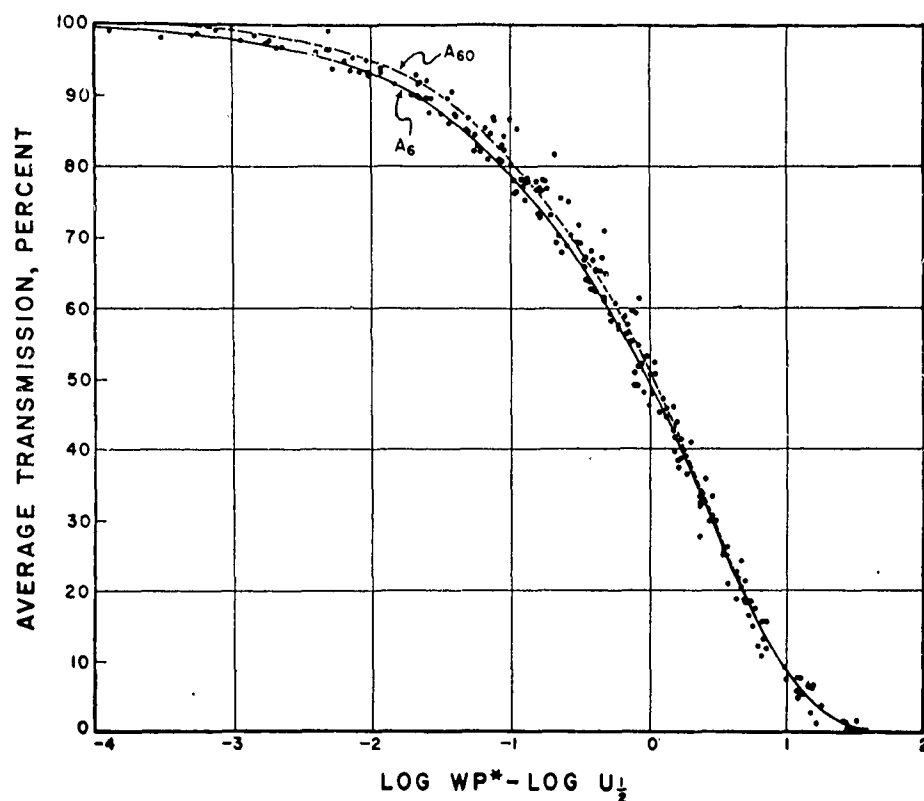


Fig. 4. — The fit of the water vapor pure rotation data to a statistical model.  $A_6$  and  $A_{60}$  refer to samples at a total pressure of 6 and 60 mm Hg, respectively.

#### HIGH RESOLUTION STUDIES OF THE SOLAR SPECTRUM

For some years the most substantial collection of high resolution spectral data relative to the infrared active constituents of the atmosphere has been the two detailed atlases of the solar spectrum recorded and compiled by Mohler and his colleagues at the University of Michigan for the spectral region 0.7 and 2.7 microns <sup>(11)</sup>, and by Migeotte et al. of the University of Liege for the spectral region 2.7 to 23 microns <sup>(12)</sup>. The Migeotte atlas had the geographic advantage that the observations were taken from the High Alpine Research Station at the Jungfrauoch, Switzerland, at an altitude of 3000 meters where the atmosphere is much drier than at sea level,

and in addition the  $\text{CO}_2$  content is also much reduced. On the other hand, even though the laboratory was well equipped, it was not practical when this atlas was prepared, to provide liquid air at the Joch or to use the more sensitive cooled detectors that are now available. Recently the group of Migeotte has been engaged in re-mapping the infrared solar spectrum from the Jungfraujoch, starting from about 0.75 microns, and a new atlas of the region 0.75 to 1.2 microns is now in publication. This region contains some 10,450 resolved lines and these have been identified and classified by O. C. Mohler of the University of Michigan and W. S. Benedict of Johns Hopkins University. The program ultimately includes the re-mapping of the entire infrared solar spectrum with cryostatically cooled infrared detectors.

#### THE WATER VAPOR CONTENT OF THE UPPER ATMOSPHERE

In many atmospheric problems it is desired to know the infrared transmission along very long slant paths in the high atmosphere. These may be problems of radiation transfer or heat balance of the earth, infrared astronomy of the atmospheres of other planets, or military problems of long range detection. The constituents  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$  and  $\text{CO}$  are generally assumed to have a uniform distribution (constant mixing ratio) with altitude. Ozone is assumed to be concentrated in a fairly narrow layer near 25 kilometers. The chief imponderable in such studies is the amount of water vapor. Until two or three years ago it was generally assumed that the stratosphere was « dry »; that is, the mixing ratio of grams of water per kilogram of air, (which at ground level is a highly variable quantity, varying between 1 and 10 g/kg), falls off at a fairly uniform lapse rate to about 0.01 g/kg at the tropopause 13-15 km. Above the tropopause it was assumed that the mixing ratio remained approximately constant at this « dry » amount. The main reason for this assumption was the lack of any suitable theoretical mechanism for the transport of water vapor through the tropopause to the higher stratosphere.

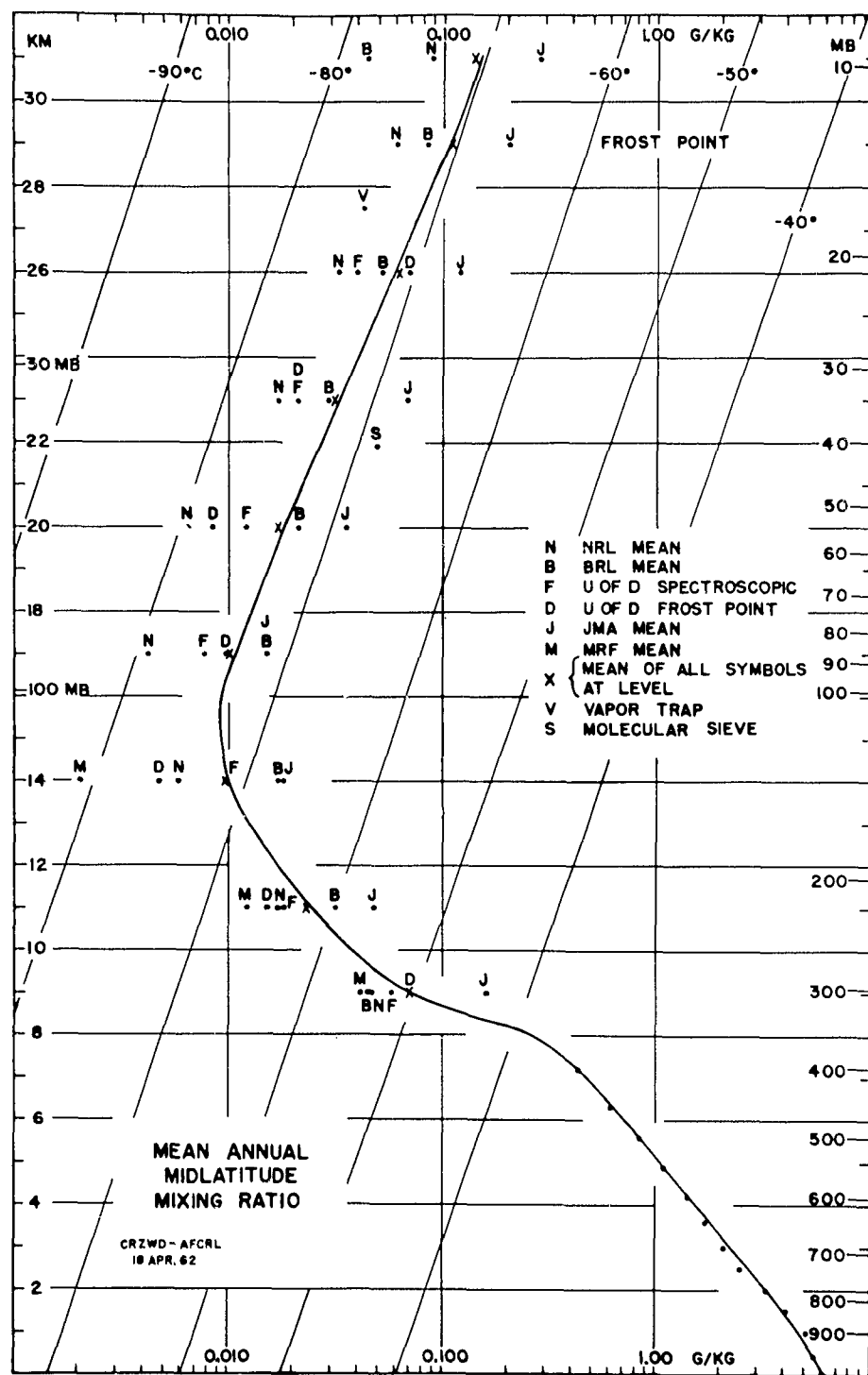


Fig. 5. — The Gutnick model for stratospheric water vapor.

However, some spectroscopic measurements of water vapor made from balloons at altitudes up to 30 km indicated a rise of the mixing ratio by at least a factor of ten from its value at the tropopause. The military designer, faced with this uncertainty, prepared infrared transmission curves for both a « dry » stratosphere (i. e. constant mixing ratio at 0.01 g H<sub>2</sub>O per kg air) and for a « wet » (saturated) stratosphere.

Gutnick has recently summarized <sup>(13)</sup> the status of our knowledge of stratospheric water vapor (Fig. 5). This summarized perhaps one hundred individual measurements made chiefly in the U. S., U. K., and Japan. There are not yet sufficient reliable data to permit estimation of variation with latitude, geography, or time of year (\*).

#### HIGH ALTITUDE INFRARED STUDIES

It was chiefly because of this debate between partisans of « wet » and « dry » stratospheres that the group of Houghton et al. commenced a broad program of high altitude studies of the near infrared atmospheric transmission, using the sun as the source of radiation. The principal results of their study is an atlas of the infrared solar spectrum from 1 to 6.5  $\mu$  observed from a high altitude aircraft, which was published in 1961 <sup>(14)</sup>. A prism-grating spectrometer utilizing a 10  $\times$  7.5 cm 300 line/mm grating and a sun-following device to keep the entrance slit illuminated was installed in a Canberra aircraft, which was capable of sustained flights at altitudes up to 15 km. The detectors used were uncooled PbS for the 1 to 3  $\mu$  region, cooled PbTe for 3 to 5  $\mu$ , and cooled PbSe for 5 to 6.5  $\mu$ . Fig. 6 is one of the 35 sections of this atlas. In each section the top curve represents records above 13 km, the

(\*) Dr. John Houghton has made spectroscopic analysis of several strong and several weak water vapor lines obtained by the RAE group. He feels that the spectroscopic evidence favors the dry stratospheric models, and that the higher water vapor amount measured from balloons probably represents outgasing from the balloon vehicle itself.

second curve 9 to 12 km and the third curve 6 to 9 km. The bottom curve is a ground-level or laboratory spectrum taken with the same spectrometer. In all cases identification is made by comparison with the Liège, Michigan and Ohio State atlases of the solar spectrum. The spectral resolution obtained was about  $1 \text{ cm}^{-1}$ .

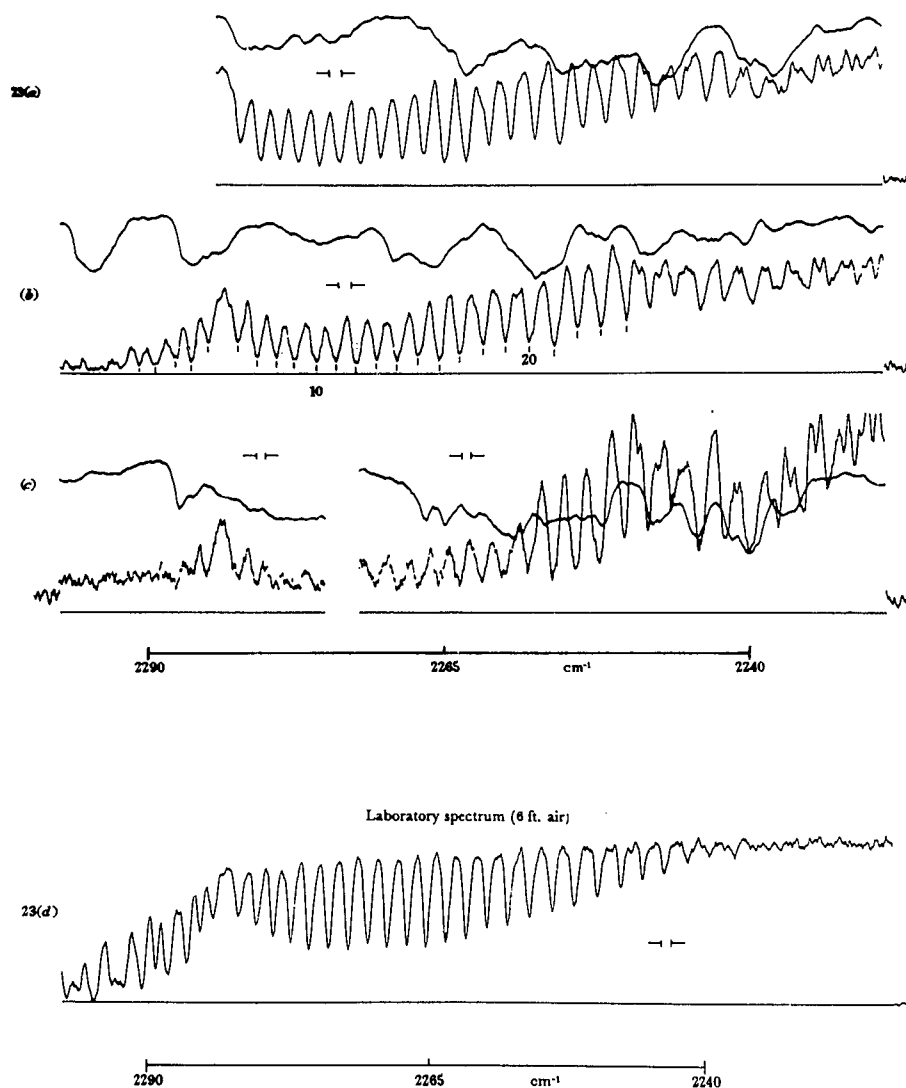


Fig. 6. — A section of the solar spectrum as observed from a Canberra aircraft

Another group studying high altitude infrared transmission from an aircraft platform is that of Cumming<sup>(15)</sup> of the Canadian Armament Research and Development Establishment, Quebec

City. This group has obtained considerable data with a lithium fluoride prism spectrometer installed in the wing pod of a CF 100 aircraft, capable of taking data up to almost 14 km. The spectrometer was recently replaced with a Perkin-Elmer 99-G spectrometer equipped with a Bausch and Lomb 300 line/mm replica grating and calcium fluoride windows. Spectra studied to date have been limited to the PbS region, and the new instrumentation has a resolution of about  $1\text{ cm}^{-1}$ , about the same as the Houghton atlas. The aim of the CARDE study is to obtain calibrated spectral data at enough different solar elevations to permit reasonably accurate determination of the solar envelope of the spectrum (i. e., the curve which would be obtained in the absence of an absorbing atmosphere) and then to determine the quantitative amounts of the atmospheric constituents as a function of altitude.

In addition to the British and Canadian airborne efforts, John Strong of Johns Hopkins University has performed some high altitude transmission studies from a U-2 aircraft at 20 km altitude (<sup>16</sup>). Because of more stringent limitations on the size and weight of the apparatus for this aircraft, the resolving power of the spectrometer was not as great as that of the instruments described above. Nevertheless some useful information was obtained on the solar envelope at high altitude.

Recently there has been an increased interest in high altitude balloon vehicles as platforms for astronomy and spectroscopy. At present the state of the art is such that 300 kg of instrumentation (including power supplies and telemetry equipment) can be lofted to 30 km, made to lock on to the sun, moon or a bright star, and remain at altitude several hours. The shortcomings of this platform are chiefly that the launching of such large balloons is very much an art. Specialized launch vehicles, tracking equipment, recovery aircraft and ground vehicles are required, and both ground and high-altitude winds and other weather conditions determine the launch time rather than the experiment on board. The shear experienced in passing through a sharp inversion layer is often sufficient to

burst a large balloon. In addition, such a balloon is considered a menace to airline navigation, and special permission must be obtained (in the U. S.) from the Federal Aviation Authority, which further restricts the possible launch times and launch sites. The ascent time must be such that the balloon is above 15 km within two hours after launch. In addition, as each new group learns to its sorrow, the low temperatures and low pressures experienced by the payload at altitude cause motors, spectrometers and tape recorders to fail and electronic circuits to behave unpredictably. It seems to be a fact of life that when the launch and balloon flight are a success the instrumentation fails, and when both of these per-

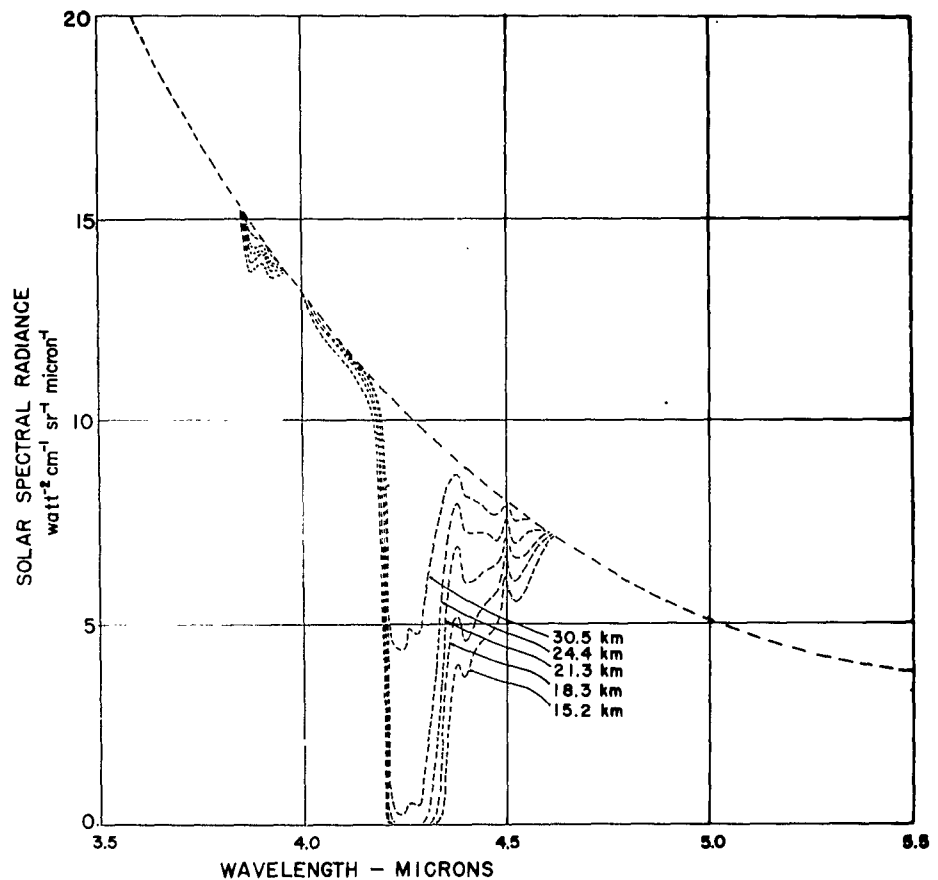


Fig. 7. — A composite spectrum of balloon-borne spectral observations of the solar spectrum in the region of the 4.3 micron carbon dioxide band from altitudes higher than 15 km.

form satisfactorily the tape recorder or telemetry fails. The problems of performing research from manned balloons are even more complex, not only because of the additional weight, but because of all of the safety requirements for the crew. Out of the last five or six attempts at major manned balloon flights there have been two fatalities, and two other narrow escapes, so that this operation remains a dangerous adventure.

In spite of all these difficulties the fact remains that the balloon and the research rocket are the only probes we have for vertical probing of the atmosphere or for sustained measurements in the environment above the 15 km altitude of aircraft and below the 100 km altitude of satellites. This region of the atmosphere has been called by some workers the *ignorosphere*. Those groups which have been most active in balloon-borne spectroscopy and astronomy include A. Dollfus in France, John Strong of Johns Hopkins University, D. Murcray of the University of Denver, M. Schwarzschild of Princeton, J. A. Hynek of Northwestern and C. Cumming of CARDE. Farmer of E. M. I. has made a useful collection of the available high altitude infrared absorption data <sup>(17)</sup>. Fig. 7 is his composite of the  $4.3\ \mu$  CO<sub>2</sub> band as observed through the atmosphere from altitudes of 15 to 30 km.

#### ABSORPTION BAND MODELS AND EMPIRICAL FORMULAE

The availability of the large body of low resolution data on atmospheric infrared absorption bands has provided material to test various theoretical models for absorption bands. The high resolution data also available for some infrared bands permits estimation of absolute or at least relative intensities for individual absorption lines or for the entire band. The goal of any science is to develop theories that will adequately represent experimental observation, which can then be used with some confidence to predict the process for conditions other than those observed.

For many practical applications in astronomy or meteorology



it is not necessary to develop a complete theoretical understanding of the absorption process, but it is adequate to formulate empirical fits to the observed data to facilitate interpolation or minor extrapolation.

For the total absorptance of infrared bands Howard et al. had developed an empirical fit of the form  $\int A_\nu d\nu = cw^{1/2}(P + p)^k$  for weak bands, and a fit of the form  $\int A_\nu d\nu = C + D \log w + K \log (P + p)$  for strong bands (where  $w$  is the absorber concentration,  $P$  the total pressure and  $p$  the partial pressure of the absorber). Burch made several improvements to these empirical fits, chiefly in the correction for self-broadening and his empirical fits have the form

$$\int A_\nu d\nu = c [w P_e^a]^b \quad (\text{weak})$$

$$\int A_\nu d\nu = C + D \log_{10} [w P_e^a] \quad (\text{strong})$$

where  $w$  is the absorber concentration (in atmos — cm),  $P_e$  is the effective pressure (in mm Hg) and  $a$ ,  $b$ ,  $c$ ,  $C$ ,  $D$  are empirically determined constants for each band. Fits such as these are intended to represent the total absorptance of the entire band, and not the resolved spectral contour. It is possible also to make empirical representations of the low-resolution spectral contour of the absorption band in terms of an empirically determined  $w_o$ , the amount of absorber concentration required to produce an absorption of 50 % at that wavelength. Both Zachor <sup>(19)</sup> and Altshuler <sup>(10)</sup> have written valuable reports giving empirical predictions of the low resolution spectral contour of atmospheric bands in terms of  $w_o$ , and with the data fundamentally based on the laboratory data of Howard and Burch and the open air data of Taylor and Yates.

Another approach in predicting atmospheric infrared transmission, is to fit the laboratory transmission data to one of the idealized models of an absorption band. The oldest model of an infrared absorption band is the Elsasser model, in which in a given spectral region the band is considered to consist of an array of regularly spaced, equally intense individual absorption lines, each having a

Lorentz shape and the same half-width. In terms of the Elsasser model one can then determine at each wavelength from the experimental data a so-called generalized absorption coefficient which varies slowly across the band. The Elsasser band model has been found useful for representing the absorption of bands such as CO, CO<sub>2</sub>, or N<sub>2</sub>O, which have a regular structure.

At the opposite extreme there is another approximate model, the so-called random or statistical model (also called the Goody or Mayer model), in which the assumption is generally retained of Lorentz shaped individual lines of equal half width, but a random distribution of line intensities or spacings between adjacent lines is assumed. This model has been found to represent the absorptance of such bands as water vapor or ozone.

There are two other band models which have been applied with some success to transmission problems and which can be considered variants of the Elsasser or random models. One originally

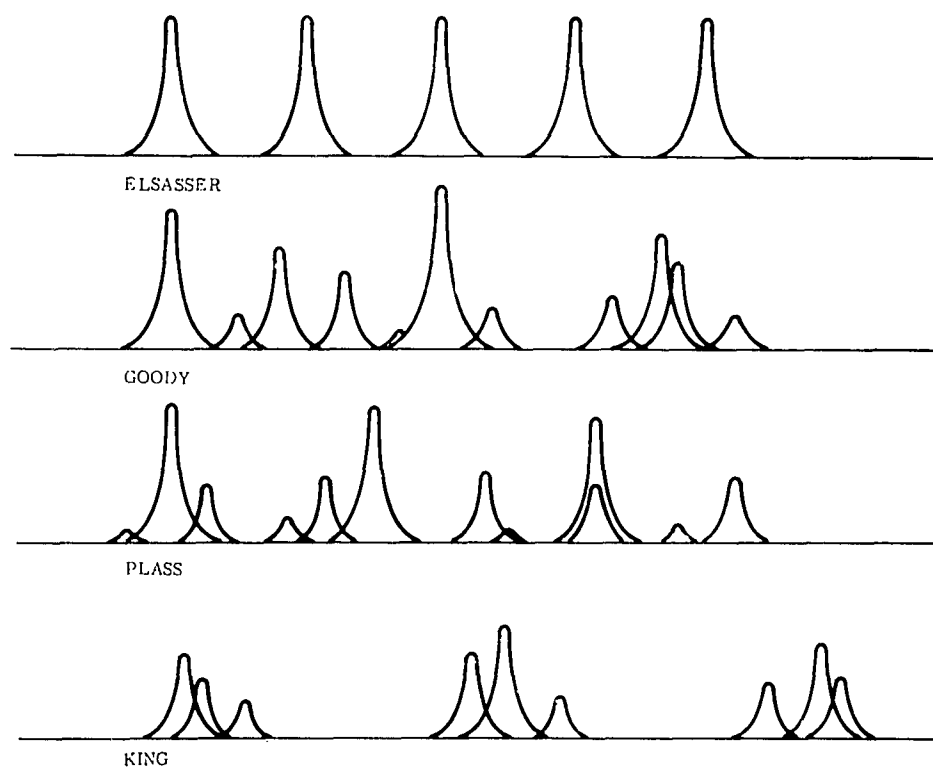


Fig. 8. — The four principal models of absorption bands.

suggested by Kaplan and utilized extensively by Plass is the so-called random-Elsasser model, in which the array of absorption lines in a given spectral region is represented by a superposition of three or four Elsasser bands of different spacing and average line intensity. The curve-of-growth of such a model can be made arbitrarily intermediate to the Elsasser or random model.

Finally, there is a model postulated by King, called the variance or clustering model, in which the lines are permitted to cluster into groups. This model has also two extremals : at one limit, the clustering of lines is a minimum when the lines are equally spaced (zero variance) which is the Elsasser model. Unit variance can be defined when the spacing is random (i. e., there is the same probability of clustering in each spectral interval) and infinite

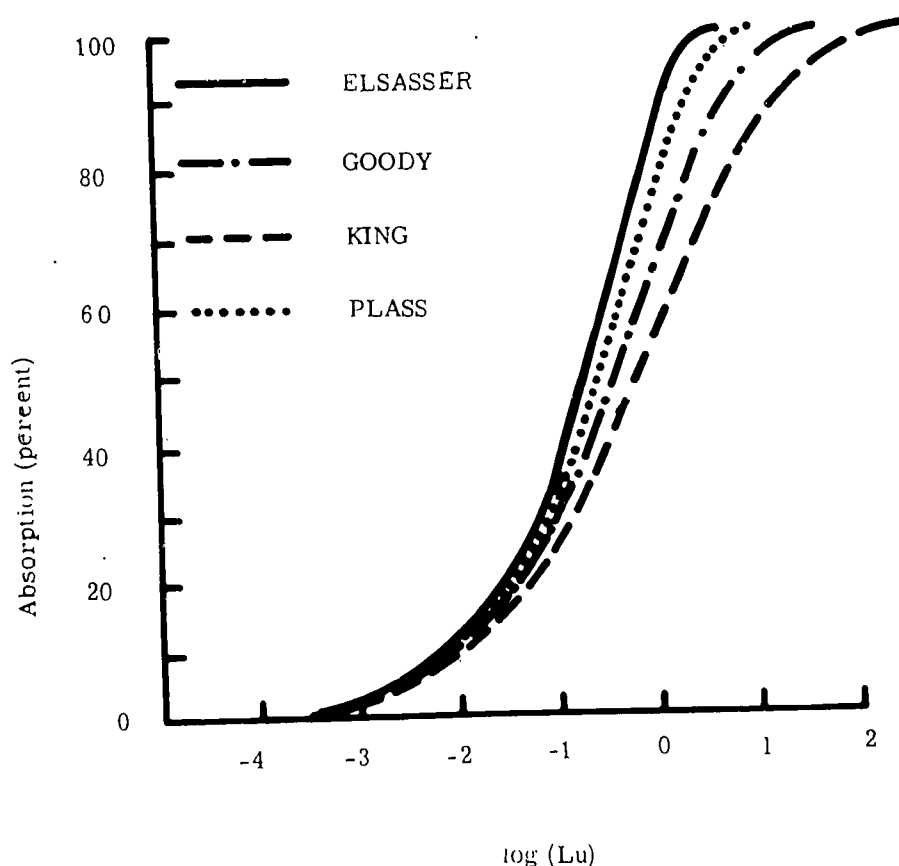


Fig. 9. — The curves of growth of the four principal models of absorption bands.

A. ELSASSER BAND MODEL

Path Length (cm)

Pressure (Atmospheres)

Transmittance

258

to other concentrations or pressure conditions with more confidence. One should however point out that there are dangers to

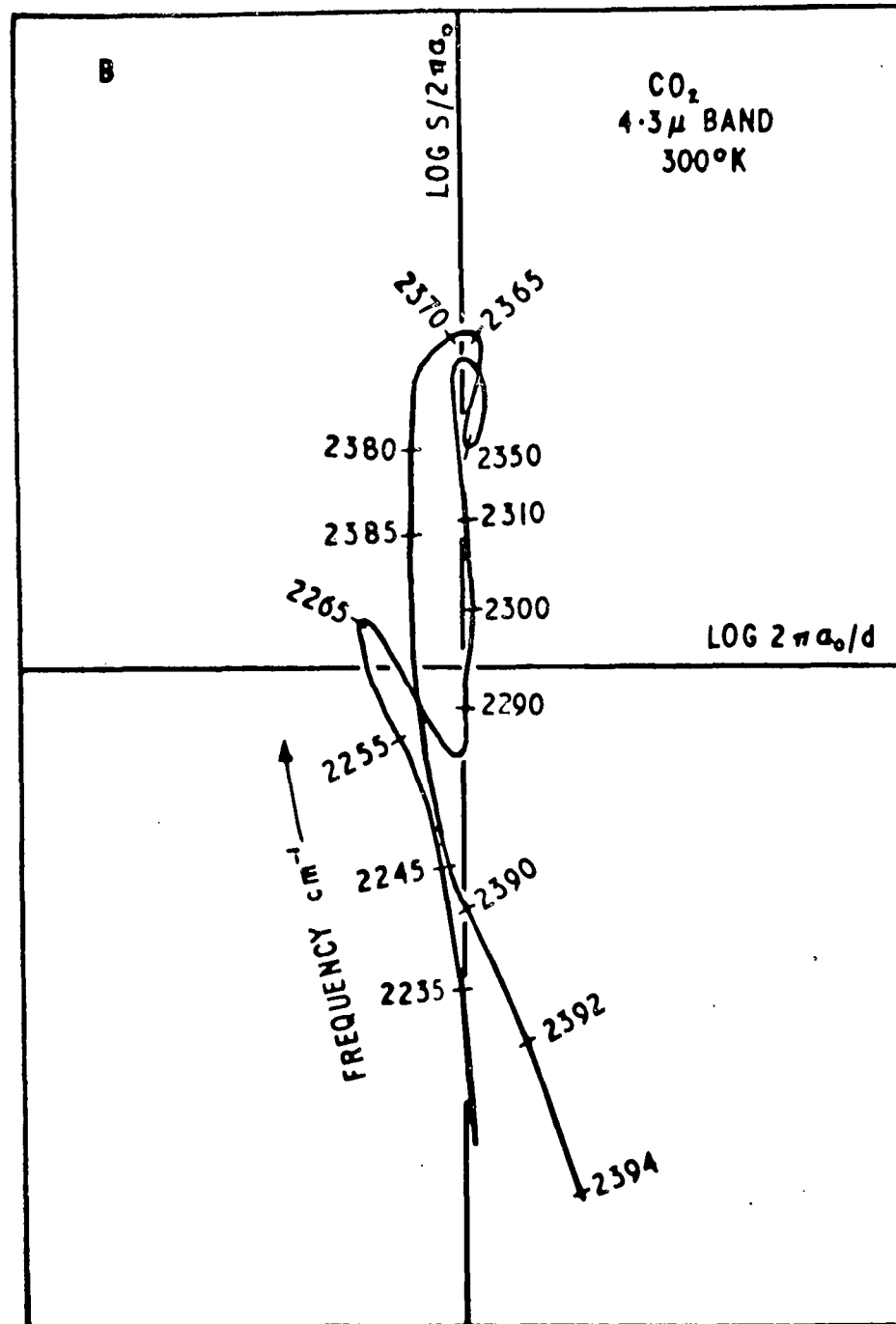


Fig. 11. — Generalized coefficients for the 4.3 micron  $\text{CO}_2$  band.

placing too much confidence in such models : in almost every theoretical model for example the variables concentration  $w$  and pressure  $P$  occur as a product  $wP$ , when the experimental data indicate that absorption varies more slowly with pressure than it does with concentration, in the form of a product  $wP^a$  where  $a$  is less than one. Fig. 8 is a generalized presentation of the four principal band models <sup>(9)</sup>, and Fig. 9 shows the curve of growth with each model. King has recently proposed yet another band model, called the modulated band absorption model.

Bradford <sup>(19)</sup> has constructed curves of generalized absorption coefficients for the Elsasser and statistical models. Fig. 10 shows the basic grid for the Elsasser band, with lines of equal transmit-

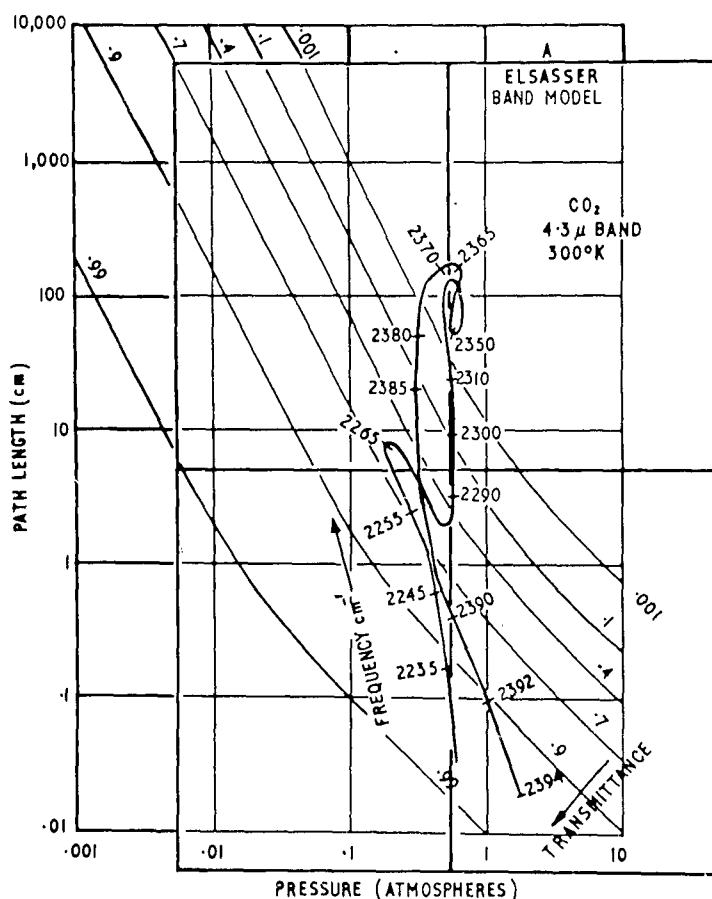


Fig. 12. — Superposition of Fig. 10 and Fig. 11 for the condition of 0.5 atm pressure and 5 cm  $\text{CO}_2$  path length.

tance shown as a function of pressure and path length. Fig. 11 shows the values of  $\log \left( \frac{2\pi\alpha_0}{d} \right)$  and  $\log \left( \frac{S}{2\pi\alpha_0} \right)$  as a function of frequency across the  $4.3 \mu$   $\text{CO}_2$  band. When these two figures are superposed as in Fig. 12, the transmittance of the  $4.3 \mu$   $\text{CO}_2$  band can be read off as a spectral function for (in this case) a path length of 5 cm  $\text{CO}_2$  and a pressure of 0.5 atm.

Stull, Wyatt and Plass<sup>(20, 21)</sup> have made an even more detailed study of the predicted transmittance for  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . High resolution data were used to determine whether the Elsasser, random-Elsasser or random model should be used in a given spectral interval, and the constants for each fit were determined throughout the infrared spectrum by normalizing against the Burch data. For  $\text{CO}_2$  the results are presented in extensive tables which give the trans-

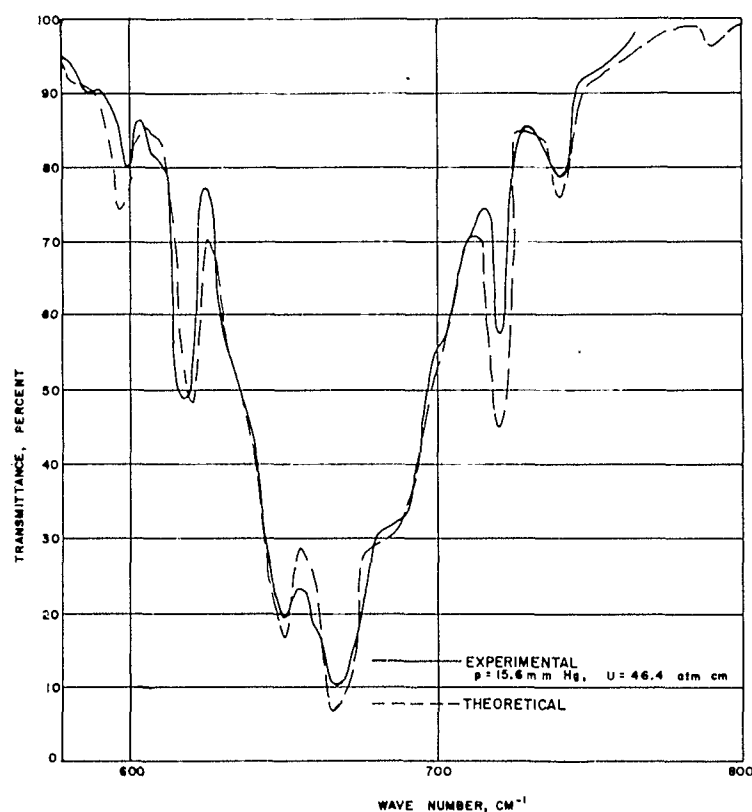


Fig. 13. — Computed spectrum of 15 micron  $\text{CO}_2$  band compared with laboratory spectrum

mission over intervals of  $5 \text{ cm}^{-1}$  and also averaged over larger intervals. Lines are included from the eight major isotopic species of carbon dioxide. For example, in the  $15 \mu$  region, 24 vibration-rotation band transitions are included for each isotopic species, and

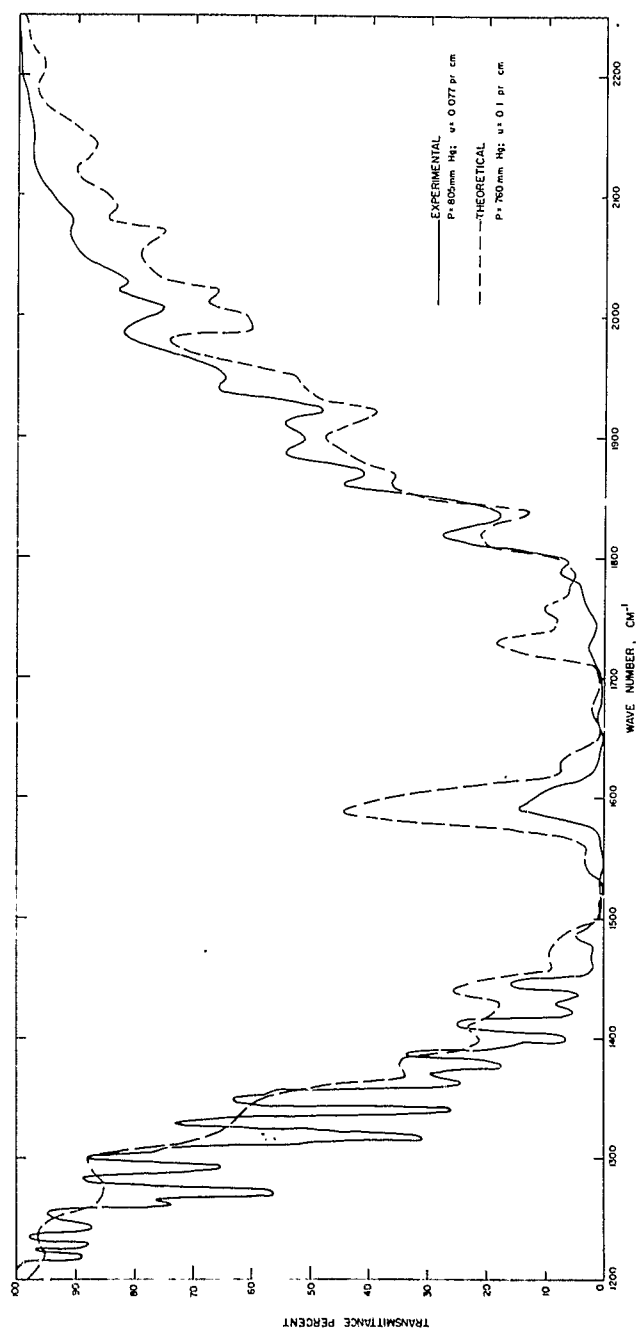


Fig. 14. — Computed spectrum of 6.3 micron bands of water vapor compared with laboratory spectrum.



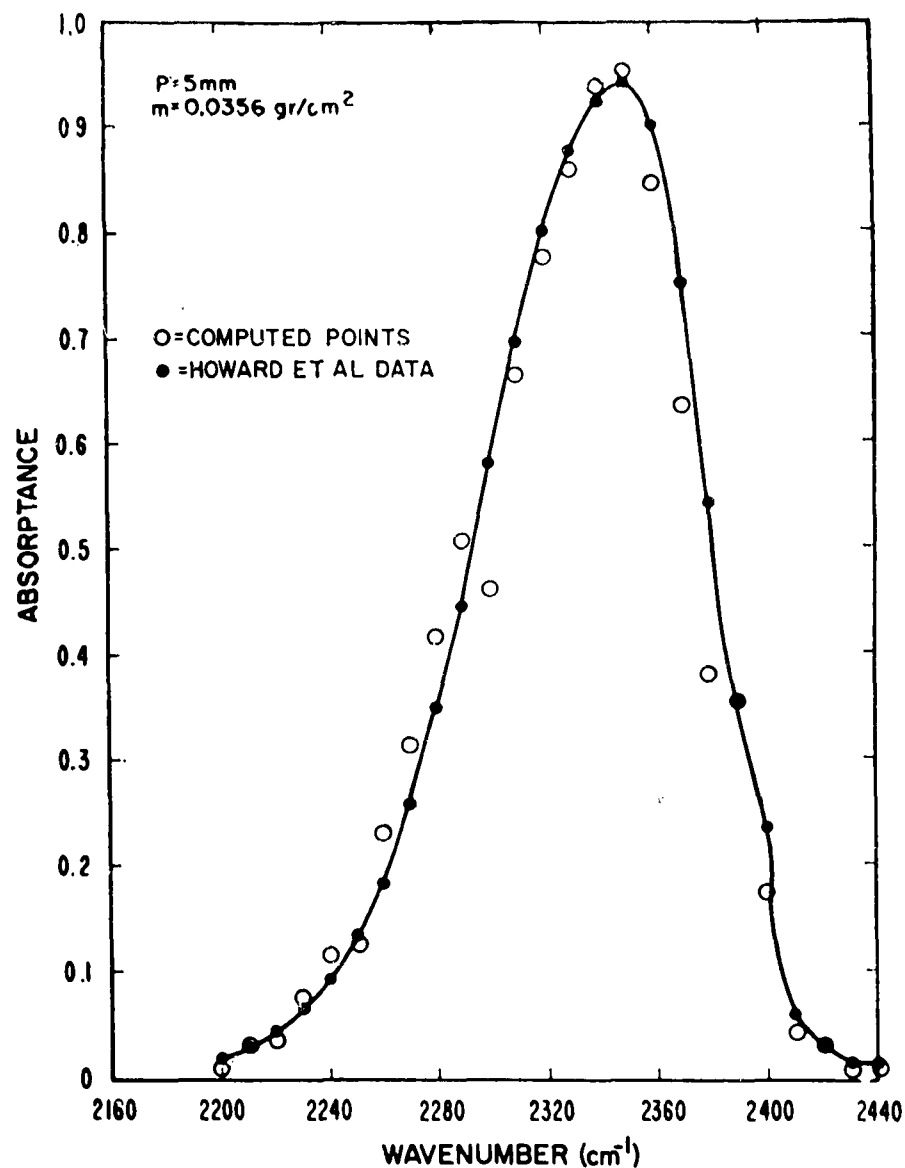


Fig. 15. — Computed spectrum of 4.3 micron carbon dioxide band compared to laboratory data.

all lines from all isotopic species having an intensity greater than  $10^{-8}$  of the strongest line in an absorption region are included in the calculation. Fig. 13 shows a comparison of the Stull, Wyatt and Plass computed spectrum and the Burch experimentally observed spectrum for the  $15\text{ }\mu$  band of  $\text{CO}_2$ .

Wyatt, Stull and Plass <sup>(21)</sup> have made a similar study of the

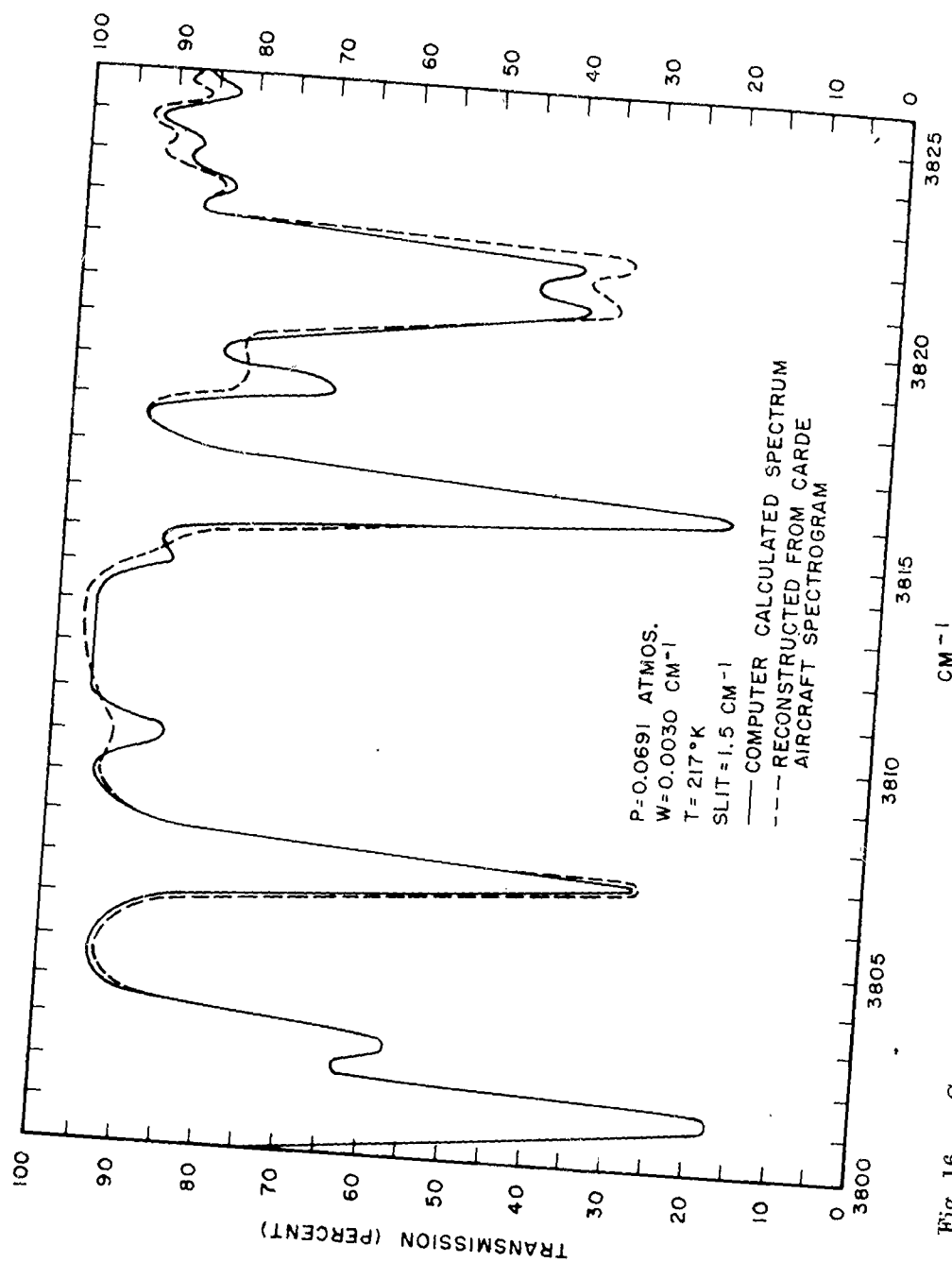


Fig. 16. — Computed curve of high altitude solar spectrum compared with observed data.

water vapor absorption spectrum. Fig. 14 shows a comparison of their predicted absorptance of the  $6.3\ \mu$  bands of water vapor with the experimental curve of Burch.

The group of Gates<sup>(21)</sup> at NBS, Boulder has similarly programmed a high speed computer to predict the infrared absorption

spectrum of water vapor and CO<sub>2</sub>. They have attempted to base their calculation on a superposition of all the positions and intensities of the individual lines as determined from the Migeotte atlas. For low resolution data they have simply fitted the Elsasser and random models to the laboratory data of Burch or the earlier Howard data. Fig. 15 shows a comparison of a predicted curve of Gates with the laboratory data of Howard for the 4.3  $\mu$  CO<sub>2</sub> band, and Fig. 16 shows a predicted high resolution high altitude curve compared with some CARDE observations. The goodness of the fit here is perhaps somewhat to be expected as the amount of water vapor in the path of the CARDE observation was not known precisely and this variable was adjusted by the computer for the best fit. Furthermore, both groups used the Migeotte atlas for their wavelength calibrations.

#### METEOROLOGICAL STUDIES

The success of the Tiros satellite and the design of more sophisticated meteorological satellites such as Nimbus has stimulated a variety of theoretical and empirical studies relating to the interpretation of atmospheric radiation data, particularly that observable in the so-called 8-13 micron window of the atmosphere. Many of these are radiation flux and emission studies, and will not be considered here, but several studies have been made of atmospheric transmission, particularly in the region of the 15 micron CO<sub>2</sub> band. Most of these have used the Ohio State University Laboratory data for the CO<sub>2</sub> and H<sub>2</sub>O vibration-rotation bands, Walshaw's data for O<sub>3</sub> and Palmer's data for the rotational H<sub>2</sub>O band, but have reworked the material into forms more convenient to use for meteorological purposes. The principal groups engaged in these meteorological studies are K. Ya. Kondratiev <sup>(23)</sup> at Leningrad, Fritz Möller <sup>(24)</sup> at Munich, Giichi Yamamoto <sup>(25)</sup> at Tohoku University, Sendai, Japan, R. Goody <sup>(26)</sup> at Harvard University, D. Q. Wark <sup>(27)</sup> of the U. S. Weather Bureau, Raymond Wexler <sup>(28)</sup>

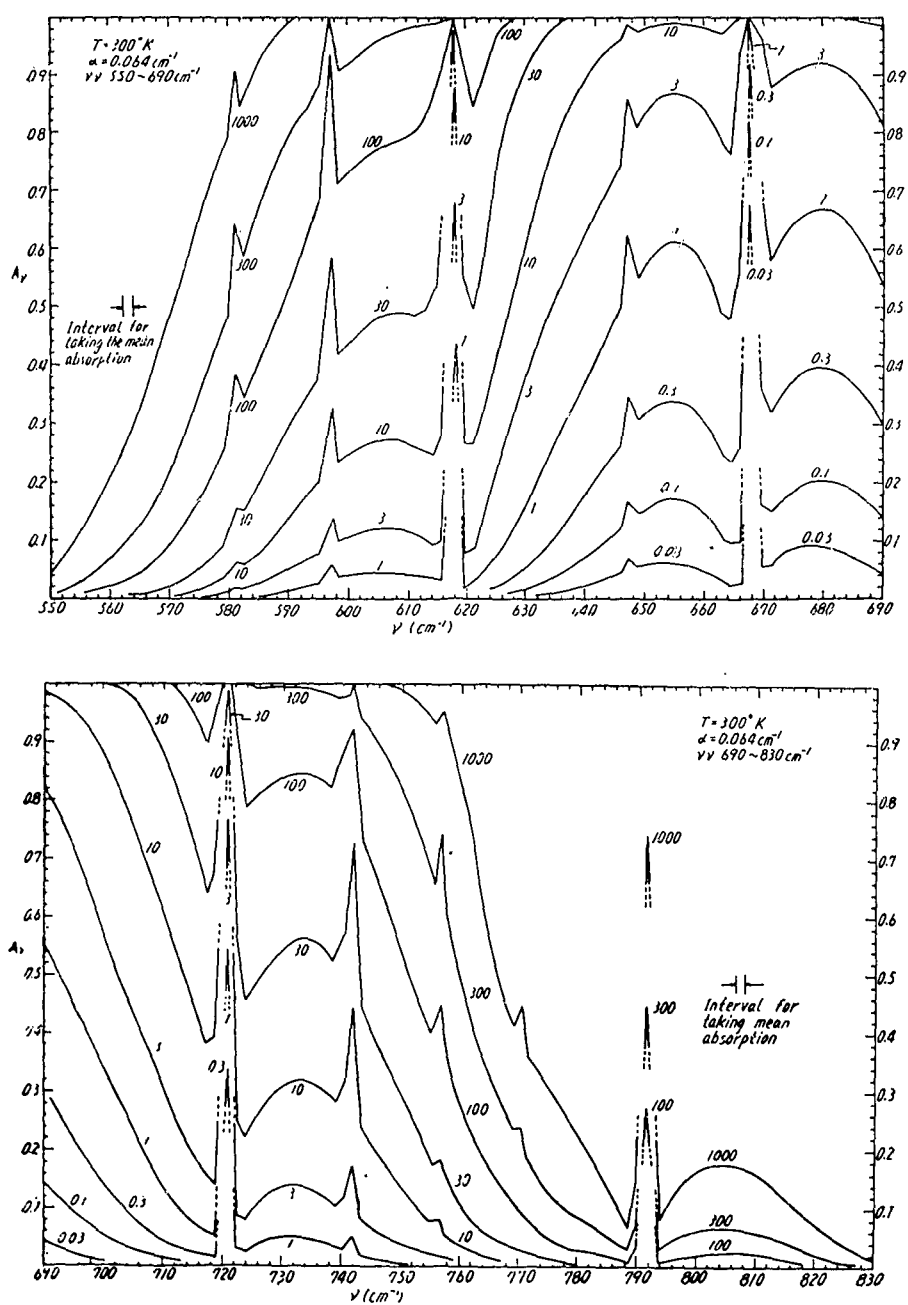


Fig. 17. — Calculated absorbance of the 15 micron  $\text{CO}_2$  band at  $T = 300^\circ\text{K}$  and  $\alpha = 0.064 \text{ cm}^{-1}$ . The figure on each curve is the pathlength in atmos — cm at NTP.

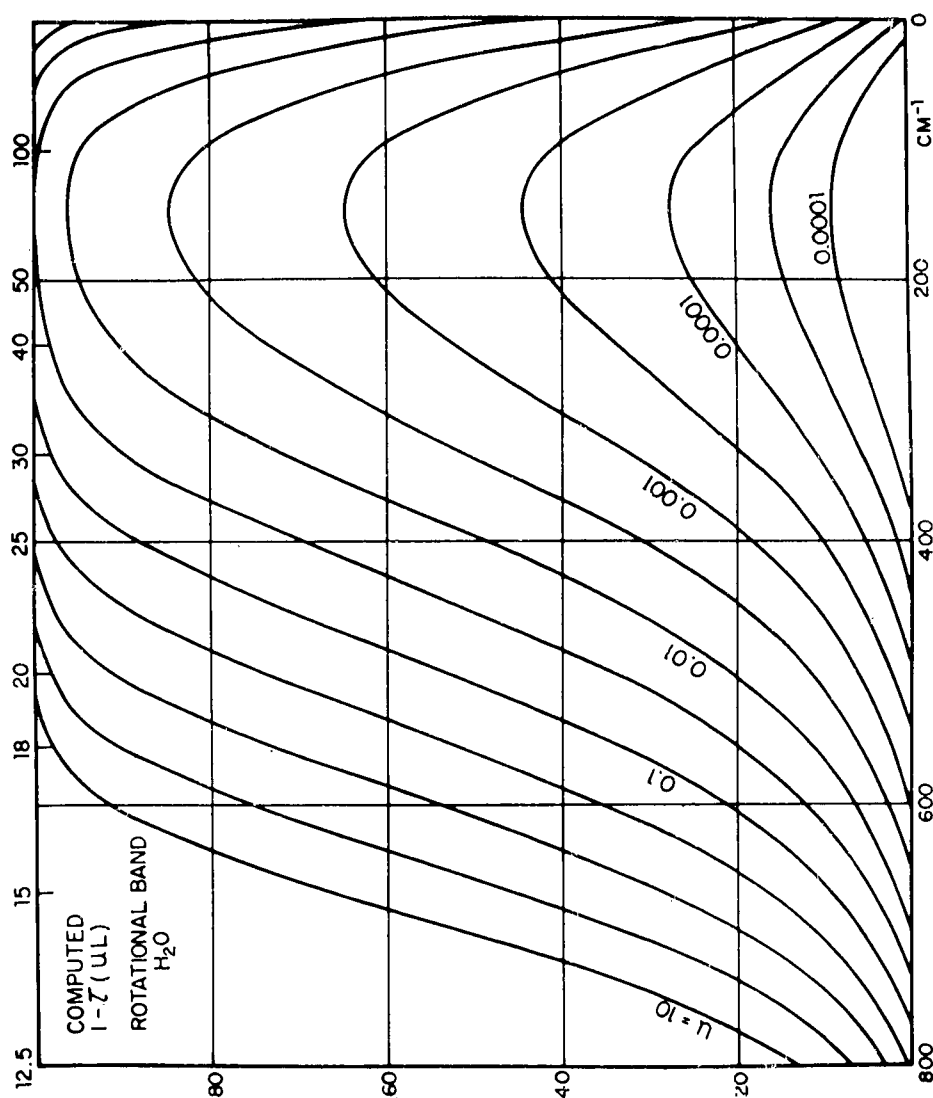


Fig. 18. — Absorbance of pure rotational water for various concentrations.

of Aracon Laboratories, Concord, Mass., and L. D. Kaplan<sup>(29)</sup> of the Jet Propulsion Laboratory. To discuss these efforts in detail would fill a large volume, indeed a book on this subject by Goody is now in press. Kondratiev<sup>(23)</sup> has now written at least three monographs on meteorological satellites. Möller<sup>(24)</sup> has published an excellent summary of all of the meteorological atmospheric transmission studies prior to 1956, and more recently has published<sup>(30)</sup> curves of the mean absorptivities of the principal atmospheric absorption bands. Yamamoto and Sasamori<sup>(25)</sup> have published

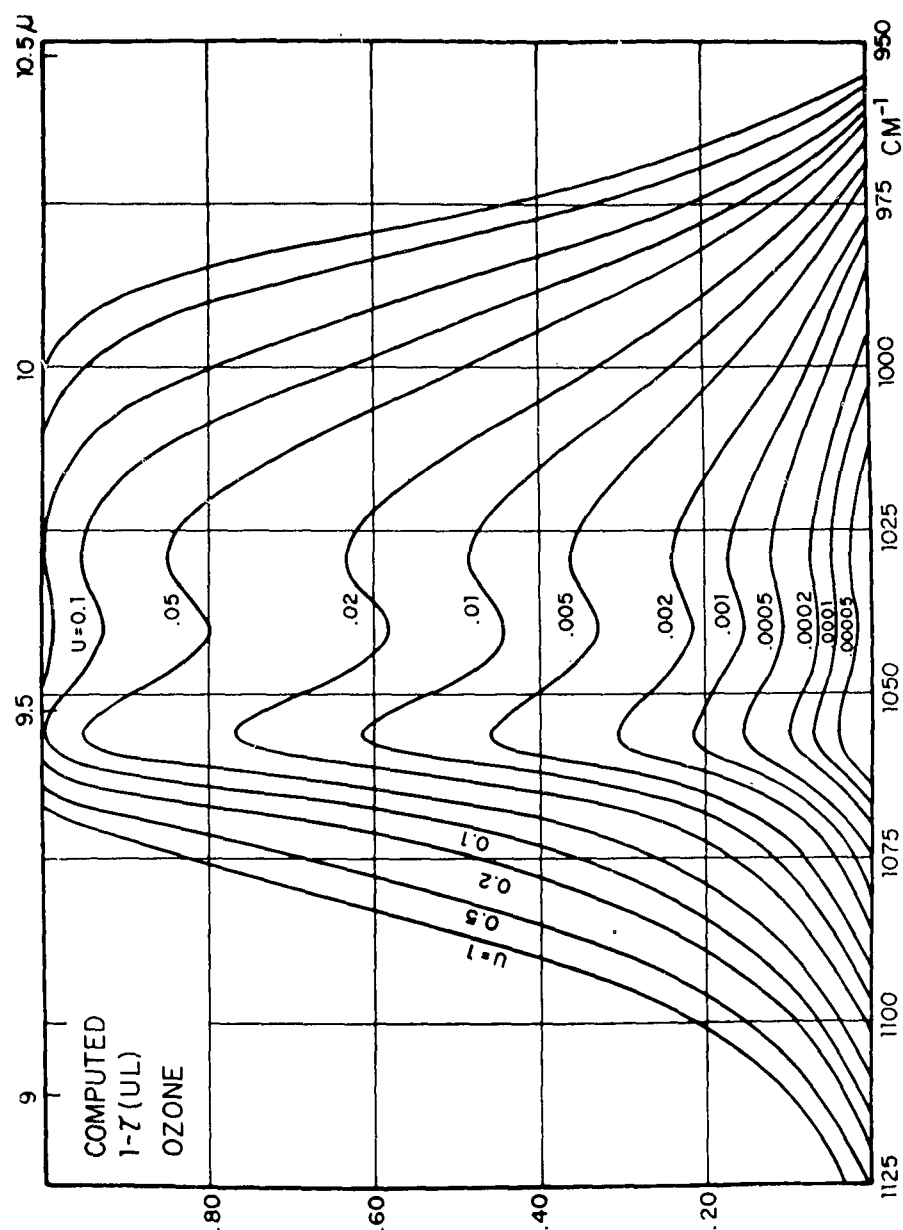


Fig. 19. — The total absorbance for the 9.6 micron band of ozone.

detailed studies on the absorption of the 15 micron carbon dioxide band. Fig. 17 shows one of their calculated representations of this band. Wark <sup>(27)</sup> has published generalized absorption coefficients for water vapor in 25  $\text{cm}^{-1}$  intervals over the region 0 to 2500  $\text{cm}^{-1}$ . Elsasser <sup>(31)</sup> has prepared a somewhat similar chart for the rotational water band, using Palmer's data, which is shown in Fig. 18.

Fig. 19 presents Elsasser's absorptance curves for the 9.6 micron band of ozone, based on the experimental data of Walshaw.

# SLANT PATHS

Many authors have considered the problems of infrared transmission along an oblique path in the atmosphere. Most of these

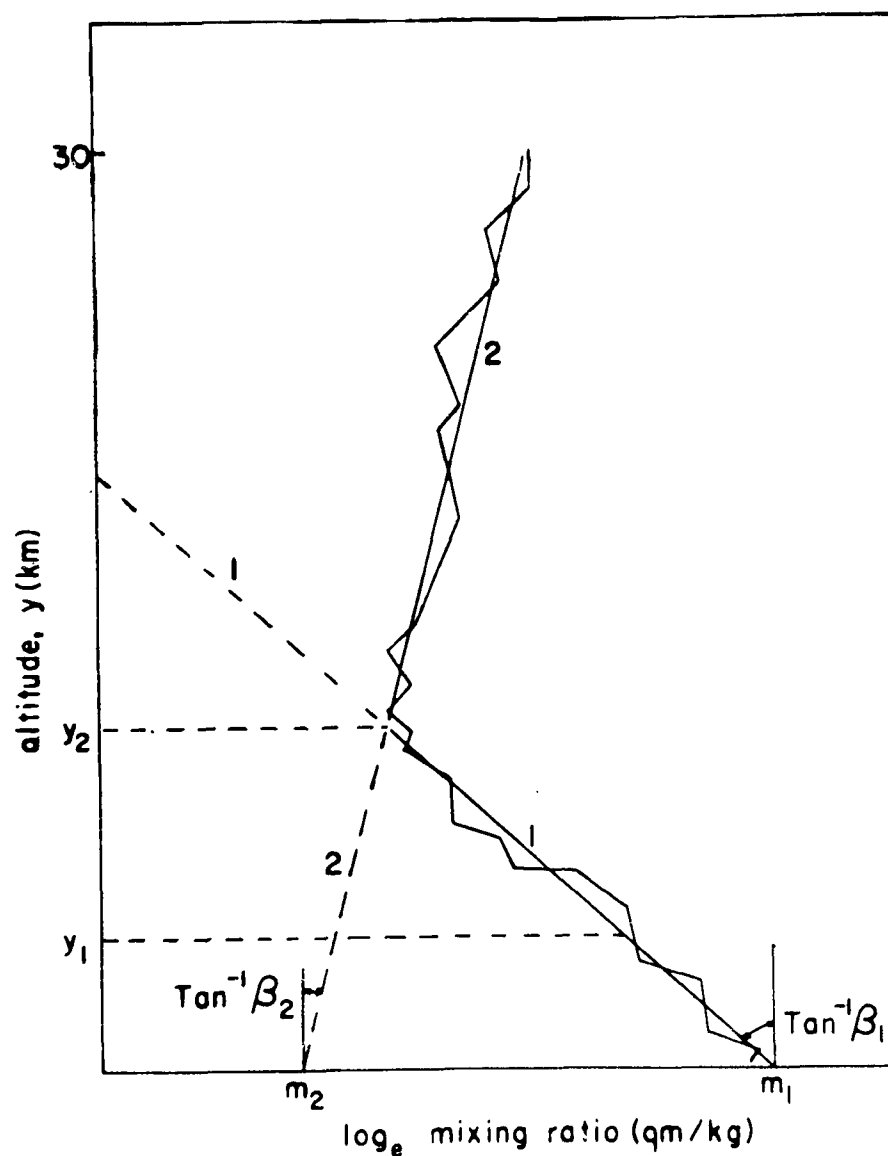


Fig. 20. — A simplified mathematical representation of the Gutnick water vapor distribution.

authors have started with the laboratory data of the Ohio State University multiple-traversal cell study, and determine a mean pressure or effective concentration along the slant path in order to apply a model such as the random or the Elsasser model. A good example of such a study is that of Plass <sup>(32)</sup>. Howard and Garing <sup>(33)</sup> recently surveyed most of these efforts and made a numerical comparison of eight of them for the predicted transmittance at 2.7 microns along a 380 km oblique path between 20 km and 87 km. They found that the predictions for this problem ranged from 15 % to 55 % transmittance, even though all of the methods were fundamentally based on the same laboratory data.

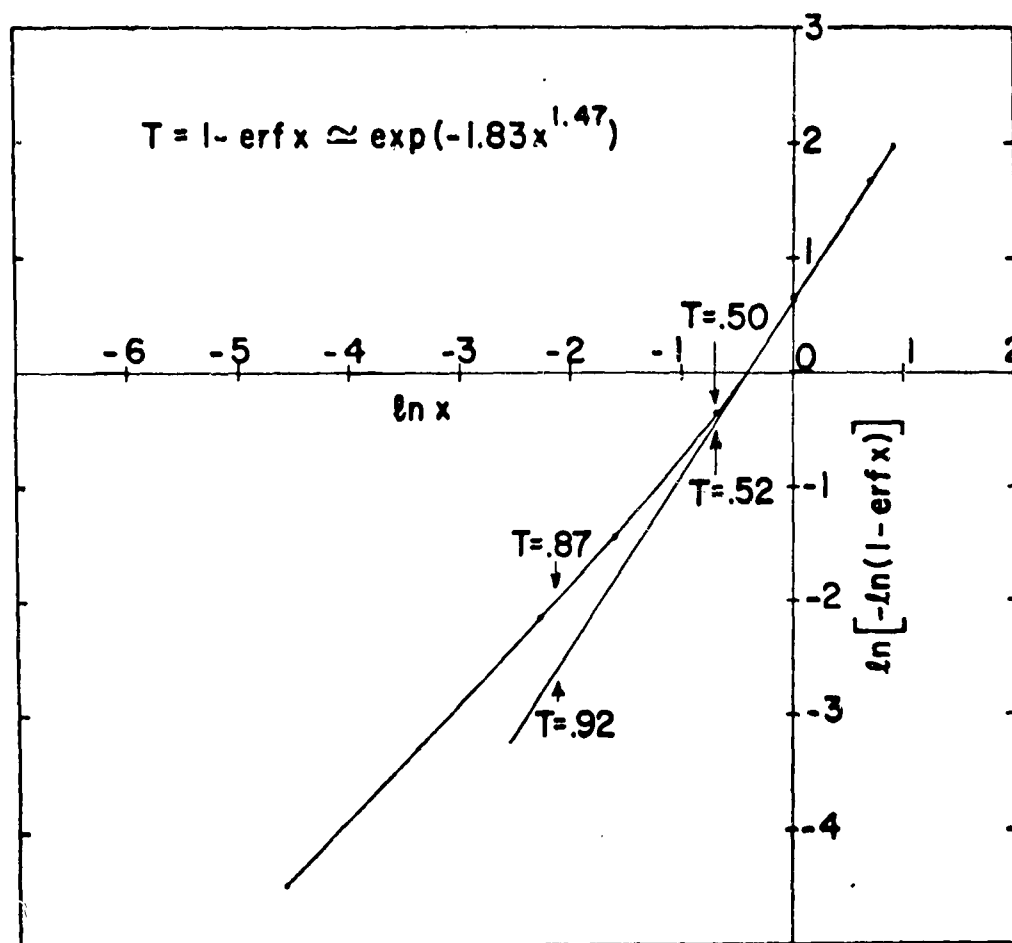


Fig. 21. — The exponential approximation to the Elsasser error function.



Shaw (34) has recently presented an empirical method for the determination of slant path transmittance which is not based on any of the theoretical band models but simply on the observed laboratory data. Green and Griggs (35) have also recently published a technique for estimation of oblique path transmission which is capable of accepting the Gutnick model of stratospheric water vapor distribution as shown in Fig. 20. They also discuss several approximations to the theory that can be used with reasonable error and that considerably simplify calculation. For example, over a rather wide range of values the error function of the Elsasser model can be approximated by an exponential function, as is shown in Fig. 21. Similarly, they have applied a simplified form of the random model, as shown in Fig 22. Green and Griggs tabulate the constants for their transmission functions for CO<sub>2</sub> and H<sub>2</sub>O over the region from 1 to 10.8 microns.

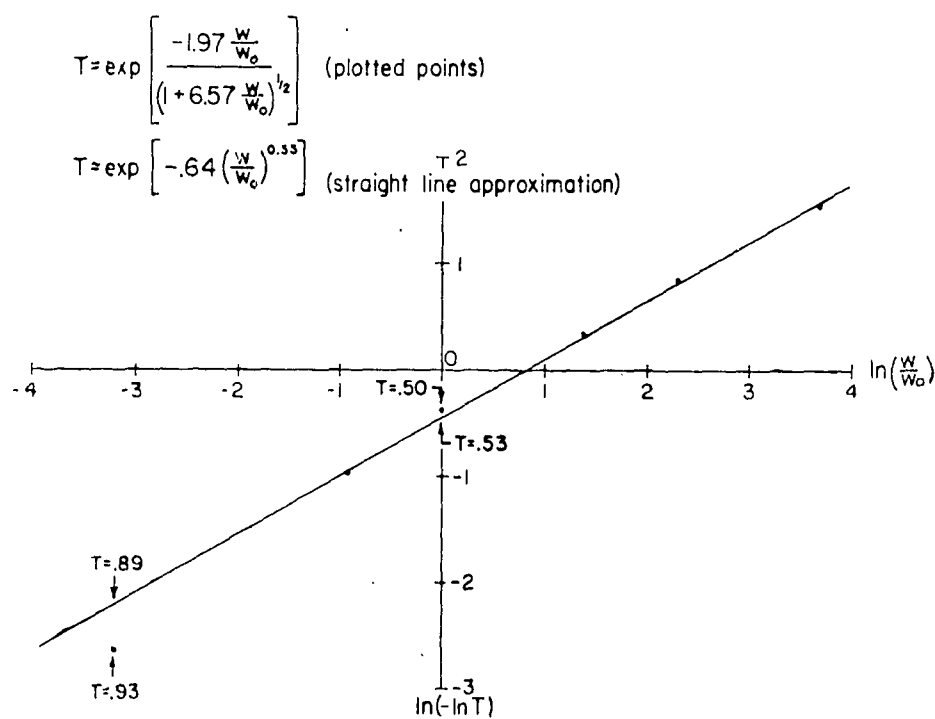


Fig. 22. — The exponential approximation to the random band model.

## HIGH RESOLUTION SPECTRUM OF OZONE

Dr. Benedict has already presented a thorough discussion of the laboratory spectral studies of most of the atmospheric molecules of interest in the infrared ; consequently, we will confine our discussion of the high resolution infrared spectra to ozone.

Considering the apparent simplicity of the molecule, namely, three oxygen atoms bound together, the determination of its three fundamental vibrations and the basic shape of the molecule resisted all efforts of analysis for many years. Finally Wilson and Badger (<sup>36</sup>) in 1948 pointed out a weak band next to the strong 9.6  $\mu$  band which they considered to be the  $\nu_1$  fundamental band.

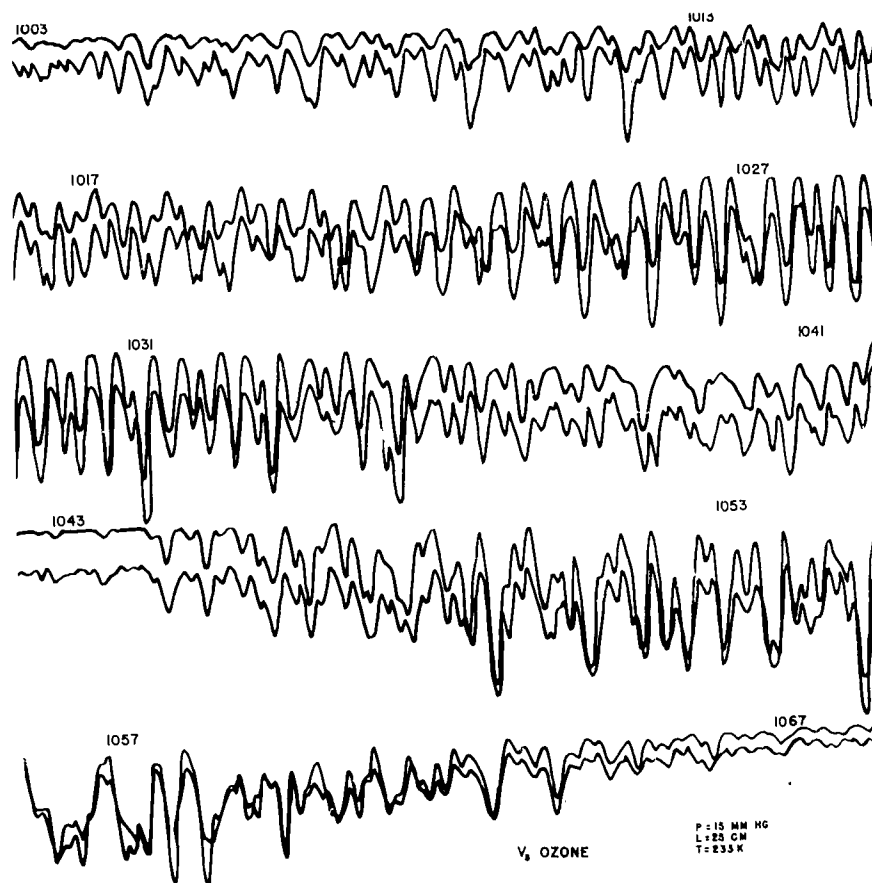


Fig. 23. — The 9.6  $\mu$   $\nu_3$  absorption band of ozone. Upper curves — theoretical, lower curves-experimental.

This then gave a consistent set of vibrational assignments to the observed bands. The high resolution rotational analysis of the individual vibration-rotation bands has also been very slow partially because of the difficulty of working experimentally with ozone and partially because the resolution required to separate the individual lines in the lower frequency bands is beyond the present capability of spectrometers..

In 1956, Kaplan, Migeotte and Neven (<sup>37</sup>), using the spectra obtained with the spectrometer then at the Jungfrauoch (<sup>12</sup>), succeeded in carrying out an analysis of the strong 9.6  $\mu$  absorption band.

Sometime later an effort was started at the Cambridge Research Laboratories to measure and analyze the weaker 9.0  $\mu$  fundamental

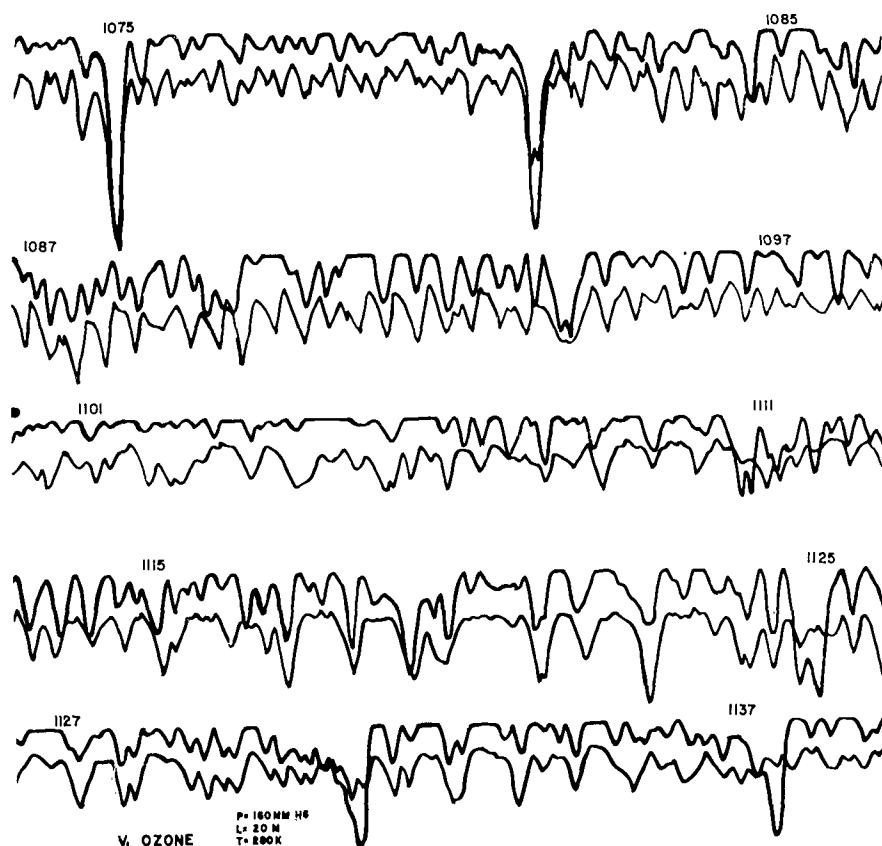


Fig. 24. — The 9.0  $\mu$   $v_1$  absorption band of ozone. Upper curves-theoretical, lower curves — experimental.

band. In order to determine which lines belonged to the  $9.6\ \mu$  band in the region common to the two bands a reanalysis of the  $9.6\ \mu$  band to higher  $J$ 's was carried out by Kneizys and Clough <sup>(38)</sup> using spectra obtained at CRL. Figure 23 gives a comparison of the theoretical spectrum (upper curve) and experimental (lower curve). Figure 24 shows the corresponding comparison for the  $9.0\ \mu$  band. Here the analysis is not so satisfactory. In particular the experimental Q branches on the high frequency end of the spectrum are weaker than the predicted ones — possibly the effect of a Coriolis interaction with the  $9.6\ \mu$  band suggested by Amat <sup>(39)</sup>.

More recently, McCaa and Shaw <sup>(40)</sup> observed the  $\nu_1 + \nu_3$  combination band at  $4.7\ \mu$  in the earth's atmosphere and in the laboratory. Using these data Trajmar <sup>(41)</sup> has carried out an analysis of the band which is illustrated in Figure 25.

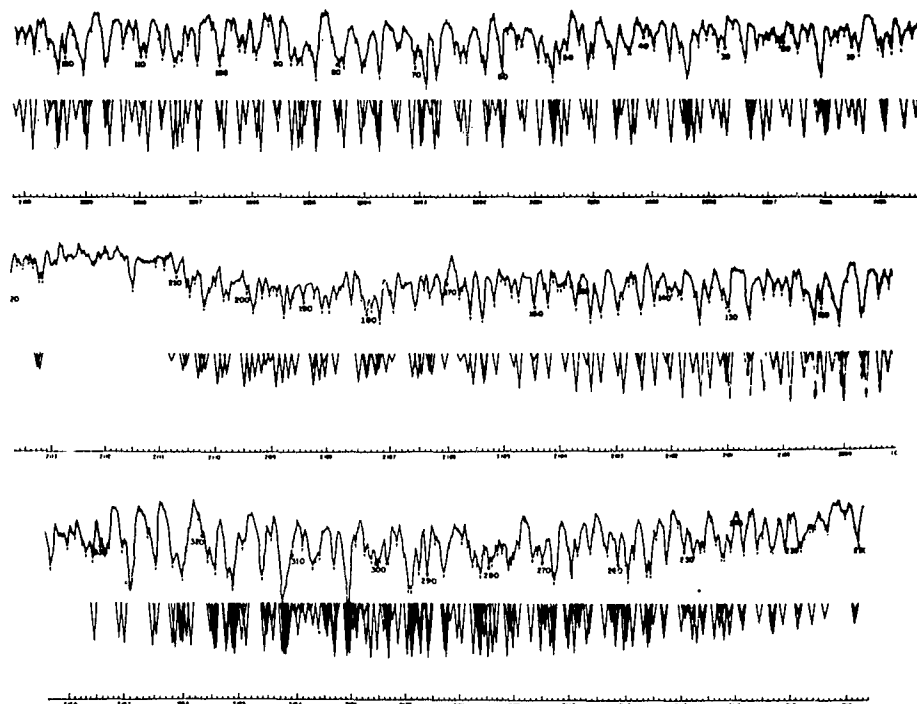


Fig. 25. — The experimental spectrum and theoretical analysis of the  $4.7\ \mu\ \nu_1 + \nu_3$  combination band of ozone.

TABLE VII

*Rotational constants for ozone.*

Ground State (cm <sup>-1</sup> )		$\nu_1$ (cm <sup>-1</sup> )	$\nu_3$ (cm <sup>-1</sup> )	$\nu_1 + \nu_3$ (cm <sup>-1</sup> )
$\nu_0$		1103.119 $\pm .009$	1042.087 $\pm .002$	2110.85
A	3.55368	3.5588 $\pm .0008$	3.5024 $\pm .0003$	3.5032
B	0.445281	0.44283 $\pm .00004$	0.44122 $\pm .00004$	0.4381
C	0.394757	0.39610 $\pm .00004$	0.38743 $\pm .00004$	0.3871

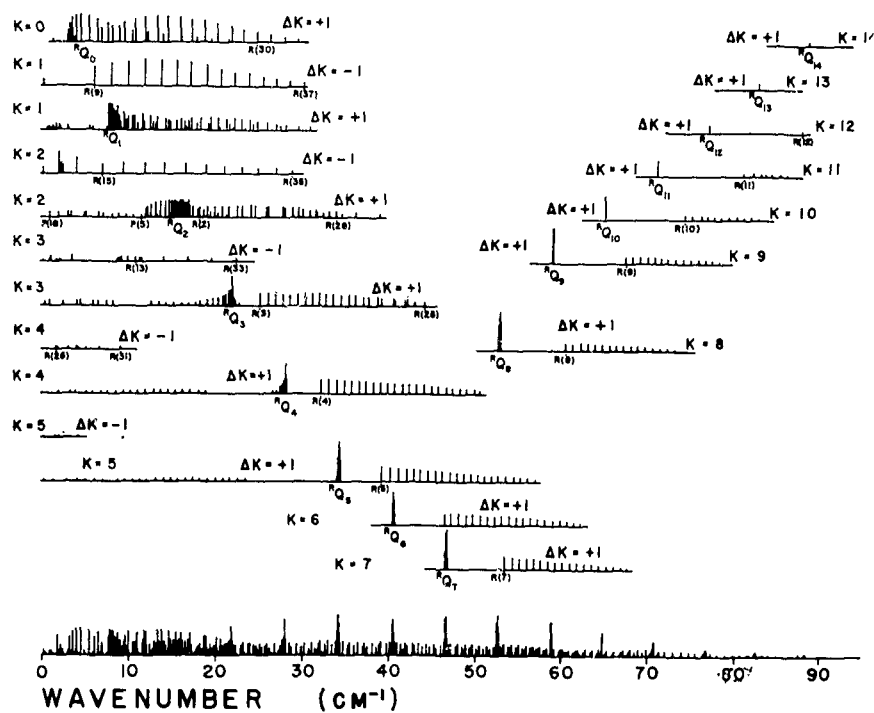


Fig. 26. — The theoretical analysis of the pure rotational band of ozone according to Gora <sup>(42)</sup> showing the separate sub-bands and the complete spectrum at the bottom.

Table VII gives the most recent constants obtained for ozone in the  $9.6\ \mu$  and  $9.0\ \mu$  bands by Kneizys and Clough and the  $4.7\ \mu$  band by Trajmar. The ground state constants are those given by Gora <sup>(42)</sup> who has carried out an extensive analysis of the pure rotational spectrum utilizing the results and microwave data of Pierce <sup>(43)</sup>, Trambarulo <sup>(44)</sup> and coworkers and Hughes <sup>(45)</sup>. Figure 26 shows the theoretical analysis of the pure rotational band of ozone by Gora.

The low frequency fundamental  $\nu_2$  at  $14\ \mu$  was most recently measured in 1955 by Nexsen <sup>(46)</sup> who made a preliminary analysis. Several laboratories are now planning to re-examine this band which will then bring up to date the analyses of the fundamental and stronger infrared ozone absorption bands.

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